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(54) PROCESS OF SKIN MELTING

(71) We, UNITED TECHNOLOGIES CORPORATION, a Corporation organized and existing under the laws of the State of Delaware, United States of America, having a place of business at 1, Financial Plaza, Hartford, Connecticut, 06101 United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:-

This invention relates to a method for producing novel and useful surface properties on a metal article, by using a concentrated source of energy to melt a thin surface layer. The rapid solidification which follows produces unique metallurgical structures.

While the metallurgical art is crowded with methods for modifying the surface properties of metal articles, most of these do not involve melting, but are solid state transformations. Although the laser has been used in the field of metallurgy since soon after its invention, the vast majority of laser metal treating operations involve either no melting, as in the transformation hardening of steel or extremely deep melting as in welding and cutting. One general exception to this is the use of lasers in surface alloying, as for example in the fabrication of wear resistant valve seats for internal combustion engines. In this specific case, surface layers, which have been enriched in certain elements, are melted under conditions of relatively low power inputs, to diffuse the surface enrichment elements into the article.

The present invention differs from several common prior art processes in conditions of absorbed power density and interaction time of the energy source and the substrate.

The technique shown as shock hardening uses extremely high power densities and short interaction times to produce a metal vapor cloud which leaves the metal surface with a high enough velocity to create a shock wave at the metal surface. Hole drilling uses a laser to produce holes in materials by vaporization of the substrate by the laser beam. Deep penetration welding uses a moderate power density and a moderate interaction time to produce deep melting in metal articles to be joined. The melting is usually accompanied by the formation of a hollow cavity which is filled with plasma and metal vapor. Finally, transformation hardening is performed at low power densities and long interaction times.

Shock hardening and hole drilling are usually performed using pulsed lasers since pulsed lasers are the most reasonable way to achieve the desired combination of power density and interaction time. Deep penetration welding and transformation hardening are usually performed using a continuous laser and the interaction time is controlled by sweeping the laser beam over the area to be welded or hardened. The present invention is concerned with skin melting. The process of the present invention involves surface melting but not surface vaporization. The prior art process areas do not reproduce the conditions of the present invention. Transformation hardening is performed at conditions where surface melting will not occur while shock hardening, hole drilling and deep penetration welding all involve a significant amount of surface vaporization.

Three references exist which describe the use of lasers in situations involving surface melting. *Appl. Phys. Letters* 21 (1972) 23-5 describes laboratory experiments in which thin surface zones were melted on noneutectic aluminum alloys using a pulsed laser. A rapid cooling rate was observed. An experiment in which metastable crystalline phases were produced by surface melting, using a pulsed laser, is described in *J. Mater. Sci.* 7 (1972) 627-30. A similar experiment in which metastable phases were produced in a series of noneutectid Al-Fe alloys is described in *Mater. Sci. Eng.* 5 (1969) 1-18.

A concentrated energy source is used to rapidly melt thin surface layers on certain alloys. Melting is performed under conditions which minimize substrate heating so that upon removal of the energy source, cooling and solidification due to heat flow from the surface melt layer into the substrate is rapid.

A flowing inert gas cover is used during the melting process so as to eliminate atmospheric contamination and to minimize plasma formation.

By controlling the heating parameters, the melt depth and cooling rate may be varied. High cooling rates may be used to produce amorphous surface layers on certain deep eutectic materials. Lower cooling rates can produce unique microstructures in transition metal base alloys which contain metalloid rich precipitates.

According to one aspect of the invention there is provided a method for producing a fine microstructure surface layer on alloys based on transition metals which contain significant quantities of metalloids including the steps of:

a. providing a metallic article having at least a surface layer based on the group consisting of transition metals and mixtures thereof further containing an amount of a metalloid material chosen from the group consisting of metalloids and mixtures thereof in excess of the solid solubility limit so that metalloid rich precipitates are present under equilibrium condition,

b. providing an energy source for producing energy having a power density in excess of about 5×10^4 watts/cm^2 the energy being absorbed and converted into thermal energy essentially at the outer surface of the article on which the surface layer is desired,

c. providing a source of a gas which is inert to the article surface material, and causing the gas to flow over the surface portion to be melted,

d. causing the energy to pass through the flowing gas and to impinge on the surface while causing relative motion between the energy source and the article surface and maintaining the flow gas cover over the portion of the surface area which is being melted, so that a shallow surface layer will be melted, without significant heating below the melted layer, with the time of exposure of a point on the surface to the energy being less than about 0.1 sec,

e. allowing the melted layer to cool by conduction into the unmelted substrate, at a rate sufficient to cause the formation of a fine microstructure surface layer wherein at least one of the average surface later crystal dimensions is less than about 1,000 Å.

According to another aspect of the invention there is provided a method for producing an amorphous surface layer on a metallic article characterized in including the steps of:

a. providing a metallic article having at least a surface layer of substantially deep eutectic composition, in which the absolute eutectic temperature is at least 15% lower than the absolute melting point of the major constituent,

b. providing an energy source for producing energy having a power density in excess of about 5×10^4 watts/sq. cm, the energy being absorbed and converted into thermal energy essentially at the outer surface of the article on which the amorphous layer is desired,

c. providing a source of a gas which is inert to the article surface layer material, and causing the gas to flow over the surface portion to be melted,

d. causing the energy to pass through the flowing gas and to impinge on the surface layer of deep eutectic composition while causing relative motion of the energy source and the article surface, while maintaining a flowing gas cover over the portion of the surface area which is being melted, so that a shallow surface layer will be melted, with the dwell time of the energy being less than about 0.1 sec, so that heating of the unmelted substrate is minimized,

e. allowing the melted layer to cool by conduction into the unmelted substrate, at a rate in excess of that required to cause the formation of an amorphous structure on the surface of the article.

Examples of the invention will now be described with reference to the accompanying drawings in which:-

Fig. 1 shows the relationship between power input, heating time, and the resultant depth of surface melt, for laser skin melting;

Fig. 2 shows the relationship between surface melt depth and an average cooling rate, for several different power inputs, for laser skin melting;

Fig. 3 shows a macrophotgraph of a partially skin melted cobalt alloy surface.

Fig. 4 shows photomicrographs of transverse sections of one of the skin melted regions of Fig. 3;

Fig. 5 shows photomicrographs of transverse sections of another of the skin melted regions of Fig. 3;

Fig. 6 shows an extraction replica from the melt zone of the material shown in Fig. 4;

Fig. 7 shows an extraction replica from the melt zone of the material shown in Fig. 5; and

Fig. 8 and 9 are extraction replicates taken within Figures 6 and 7 respectively;

Skin melting is a term which has been coined to describe the rapid melting and solidification of a thin surface layer on the surface of a metallic article as a result of high concentrated energy inputs to the surface. By putting energy into the surface layer at a high enough rate, at a rate which greatly exceeds the rate at which heat can be conducted into the material, the temperature of the surface layer can be raised to above its melting point without significantly increasing the temperature of the underlying bulk substrate, that is to say, high energy inputs can produce steep thermal gradients. Thus, when the energy input to the surface is terminated, the thermal energy heat in the melted surface layer will be rapidly dissipated into the cool underlying substrate. Calculations and experiments indicate that cooling rates in excess of about 10^5°C per second may be achieved for melted surface layers which are on the order of 25.4 to 50.8 microns in thickness. Of course, the parameters and effective cooling rates generated by the skin melting technique will vary with the thermal properties of the material.

The energy source must satisfy certain criteria. The first criterion is that the energy source must be capable of producing an extremely high absorbed energy density at the surface (i.e. in excess of 5 x 10^4 watts/sq cm). For this process, the critical parameter is absorbed energy rather than incident energy. For the case where a laser is used as the energy source, and this is one of the few known energy sources capable of generating the necessary energy densities, the propertion absorbed varies widely with differences in material and surface finish. Another phenomena which reduces absorbed power is the plasma cloud which forms near the surface during laser irradiation. This plasma cloud absorbs some of the incident energy and also caused defocusing of the beam thus reducing the power density. The second criterion is that the absorbed energy must be essentially completely transformed into thermal energy essentially at the outer surface of the article. This criterion must be observed in order to ensure that excessive heating of the substrate, and consequent reduction of the cooling rate, do not occur. Subject to this second criterion, electron beam (E.B.) heating may also be used.

Briefly, the invention process is performed as follows: a continuous energy source, having characteristics to be defined below, is used to heat the surface of the article to be treated. Although electron beam techniques may be used, a continuous wave laser is the preferred source. When a laser is used, the point of interaction between the beam and the surface is shrouded with a flowing inert gas to minimize interaction of the surface melt zone with the atmosphere, and to reduce plasma formation. The energy source is then moved relative to the surface to produce the skin melting effect on a continuous basis. Overlapping passes may be used to completely treat an article surface.

Based on the intuitive feeling that such a process might result in cooling rates sufficiently high to produce nonequilibrium structures, even noncrystalline structures, experiments were performed which verified this concept. A computer program using finite element heat flow analysis was then developed and utilized to predict the cooling rates which should be obtained in a particular material (pure nickel) as a function of different conditions.

Fig. 1 shows the interrelationship between absorbed power, duration of power application and resultant melt depth. This figure is based on the thermal properties of pure nickel and assumes that the power source is a laser beam which is absorbed at the surface. The figure has two sets of curves, one relating to absorved power (watts/sq. cm.) and the other relating to absorbed energy (joules/sq. cm.). For example it can be seen that if a laser beam with a density sufficient to cause a power absorbtion of 1 x 10^6 watts/sq. cm. were applied to a nickel surface for a time of 10^{-5} seconds, the resultant melt depth would be slightly less than 10^{-1} mils [2.54 microns]. Likewise, if a laser beam were used to cause an energy of 1 joule/sq. cms. to be absorbed by a nickel surface in a time of about 10^{-7} seconds, a surface melt depth of slightly less than 10^{-2} mils (0.25 microns) would result. This curve points out that when high absorbed power densities are applied to metallic surfaces, controlled melting of surface layers can occur quite rapidly. The energy source used is preferably continuous and is moved relative to the surface being treated. The approximate dwell time may then be calculated from the relationship

$$\text{dwell time} = \frac{\text{spot size}}{\text{rate of relative motion}}$$

The dwell time is less than about 0.1 second.

F i g

Fig 2 shows another family of curves which relate melt depth and absorbed power density to the average cooling rate of the surface melt layer between the melting point and 1500°F (816°C). With regard to the example mentioned above, in connection with Fig. 1, of a beam which causes a power absorbtion of 10^6 watts/sq. cm., applied to the surface for a time 10^{-5} seconds, to produce a melt depth of indicates that under these conditions the average cooling rate of the melt layer would be about 5 x 10^8°F/sec (277.10^6°C/sec). These cooling rates assume a thick substrate. Such cooling rates are extremely high and can be utilized to produce new and novel microstructures in certain materials.

A certain class of materials, defined as deep eutectic materials, may be made amorphous, when the skin melting conditions are sufficient to produce cooling rates in excess of about 10^{6}°F/sec (5.5 10^{5}°C/sec). and preferably in excess of about 10^{7}°F/sec (55.10^{5}°C/sec). A eutectic composition is a mixture of two or more elements or compounds which has the lowest melting point of any combination of these elements or compounds and which freezes congruently. For the purposes of this invention a deep eutectic is defined to be one in which the absolute eutectic temperature is at least 15% less than the absolute melting point of the major eutectic constituent. Referring to Fig. 2 it can be seen that a cooling rate in excess of 10^{6}°F/sec. 5.5.10^{5}°C/sec) requires an absorbed power density in excess of about 5 x 10^{4} watts/sq. cm., and can only be achieved in melt depths of less than about 5 mils (72.4 μ). Amorphous surface layers have been obtained in alloys based on the eutectic between palladium and silicon (in a $Pd_{0.775}$-$Cu_{0.06}$-$Si_{0.165}$ alloy) in which the absolute depression of the eutectic temperature (1073°K), from the absolute melting point of palladium (1825°K) is about 41%. In both this embodiment and the one which follows, the surface layer may or may not have the same composition as the underlying substrate material. A modified composition surface layer may be produced by many techniques known in the metallurgical art including:

a. completely different surface layers may be applied by a variety of techniques which include plating, vapor deposition, electrophoresis, plasma spraying and sputtering. The surface layers thus applied are preferably of substantially eutectic composition and need not have any constituents in common with the substrate.

b. a layer of an element which forms a eutectic with a major element in the substrate may be applied and then caused to diffuse into the substrate by appropriate heat treatments in the solid state. The material may be applied by a wide variety of techniques which include the techniques set forth above in "a".

c. a layer comprised in whole or in part of a material which forms a deep eutectic with a major constituent of the substrate may be applied to the surface of the substrate and melted into the substrate by application of heat, as for example by laser or electron bean, so as to form a surface layer of the desired depth of substantially eutectic composition.

The second class of materials which may be treated by the present process are alloys based on transition metals and which contain an amount of a metalloid in excess of the solid solubility limit. The term metalloid as used herein encompasses C, B, P, Si, Ge, Ga, Se, Te, As, Sb and Be (which although not technically a metalloid behaves in a similar fashion). Preferred metalloids are C, B and P with B and P being most preferred. Preferred transition elements are Fe, Ni and Co. Under the cooling conditions which result from normal melting and cooling (i.e. rates less than about 10^{3}°F/sec (5.5$10^{2}$°C/sec) such alloys contain massive, metalloid-rich particles (having dimensions on the order of microns). Although techniques to control particle morphology during solidification have been developed, notably directional solidification, the dimensions and spacing of the metalloid rich particles are still on the order of microns. By applying the present invention process to this class of alloys the size of the metalloid rich precipitates can be reduced to less than 0.5 microns and preferably less than 0.1 microns. The cooling rates necessary to effectuate such a microstructural change is at least 10^{4}°F/sec (5.5$10^{3}$°C/sec) and preferably at least 10^{5}°F/sec (5.5 10^{4}°C/sec. From figures 1 and 2, cooling rates of 10^{4}°F/sec. (5.5 10^{3}°C/sec and 10^{5}/sec. (5.5$10^{4}$°C/sec) can be seen to require power densities of about 5 x 10^{3} and 2 x 10^{4} watts/sq. cm., respectively. This aspect of the invention may be understood by reference to the figures. Figure 3 shows a planar view of a cobalt alloy (Co-20% Cr-10% Ni-12.7% Ta-. 75%C) which has been skin melted under the conditions indicated. Prior to skin melting the alloy had been directionally solidified to produce a structure which includes TaC fibers in a cobalt solid solution matrix. Figures 4 and 5 are transverse photomicrographs of two of these skin melted passes. Figures 6 and 7 are also transverse views, at higher magnification, showing that the carbide (TaC) fiber (dark phase) spacing is about 5-10 microns. Figures 8 and 9 are extraction replicas taken from within the skin melted regions of figures 6 and 7, illustrating the changes in carbide morphology which result from skin melting. Because melt depth in Fig. 5 is deeper than in Fig. 4, the Fig. 4 material experienced a higher cooling rate. The dark carbide particles in Fig. 6 are essentially equiaxed and probably formed by precipitation from a super-saturated solid solution after solidification. The carbide size is about .1 microns. Fig. 4 illustrates a different structure, a filamentary carbide structure formed during solidification. The filaments are about 1-2 microns long and about 500A° in diameter. Such structures are extremely hard and are believed unique. Unlike the amorphous layers described earlier, they are relatively stable and not subject to extreme structural changes at elevated temperature. In an alloy based on the nickel-4% bornon eutectic, Vickers hardnesses of over 1200 kg/mm^{2} have been obtained, harder than the hardest tool steels known. In the process of the present invention, the melt layer is comparatively thin. For this reason, any reaction of the melt with the environment should be avoided, since any surface cleaning process would probably remove a significant portion of the surface layer. Likewise, the present invention depends on controlled surface melting, and any factor which interferes with close control of the melting process should be avoided. When a laser is used as an energy source for the present invention, certain adverse phenomena occur at the point of interaction between the laser beam and the surface being treated. The major adverse reaction is the formation of a plasma cloud. This cloud absorbs a fraction of the beam, reflects another fraction of the beam and tends to defocus the remaining portion of the beam thereby lessening the incident energy density. Because of the factors discussed above, a flowing inert gas cover is an important part of the present process when a laser is the energy source. This gas serves to eliminate adverse surface-environment reaction, and minimizes plasma formation. The gas used should be essentially nonreactive with the (molten) surface layer and should flow at a rate of at least 2 feet per minute (0.60m/min) at the point of laser-surface interaction. Excellent results have been obtained with a helium-argon mixture at flow velocities of from 2-20 feet per minute (0.60 - 6.0 m/min).

Although the invention has been shown and described with respect to a preferred embodiment thereof, it should be understood by those skilled in the art that various changes and omissions in the form and detail thereof may be made therein without departing from the scope of the invention.

WHAT WE CLAIM IS:

1. A method for producing an amorphous surface layer on a metallic article characterized in including the steps of:

a. providing a metallic article having at least a surface layer of substantially deep eutectic composition, in which the absolute eutectic temperature is at least 15% lower than the absolute melting point of the major constituent,

b. providing an energy source for producing energy having a power density in excess of about $5x10^4$ watts/sq. cm. the energy being absorbed and converted into thermal energy essentially at the outer surface of the article on which the amorphous layer is desired,

c. providing a source of a gas which is inert to the article surface layer material, and causing the gas to flow over the surface portion to be melted.

d. causing the energy to pass through the flowing gas and to impinge on the surface layer of deep eutectic composition while causing relative motion of the energy source and the article surface, while maintaining a flowing gas cover over the portion of the surface area which is being melted, so that a shallow surface layer will be melted, with the dwell time of the energy being less than about 0.1 sec, so that heating of the unmelted substrate is minimized,

e. allowing the melted layer to cool by conduction into the unmelted substrate, at a rate in excess of that required to cause the formation of an amorphous structure of the surface of the article.

2. A method according to claim 1 wherein the absolute eutectic temperature of the surface layer is depressed by at least about 25% from the absolute melting temperature of the major eutectic constituent.

3. A method according to claim 1 or claim 2 wherein the energy source is a continuous laser.

4. A method according to claim 1 or claim 2 wherein the energy source produces an electron beam.

5. A method according to any one of claims 1 to 4 wherein the gas flows over the surface at a velocity in excess of about 2 feet per minute (0.60 m/min).

6. A method according to any one of claims 1 to 5 wherein the depth of the surface layer is less than about 5 mils (127 μ).

7. A method according to any one of claims 1 to 6 wherein the resultant cooling rate is in excess of about 10^{6}°F/sec (5.5×10^{5}°C/sec).

8. A method for producing a fine microstructure surface layer on alloys based on transition metals which contain significant quantities of metalloids including the steps of:

a. providing a metallic article having at least a surface layer based on the group consisting of transition metals and mixtures thereof further containing an amount of a metalloid material chosen from the group consisting of metalloids and mixtures thereof in excess of the solid solubility limit so that metalloid rich precipitates are present under equilibrium conditions,

c. providing an energy source for producing energy having a power density in excess of about $5x10^4$ watts/cm^2 the energy being absorbed and converted into thermal energy essentially at the outer surface of the article on which the surface layer is desired,

c. providing a source of a gas which is inert to the article surface material, and causing the gas to flow over the surface portion to be melted,

d. causing the energy to pass through the flowing gas and to impinge on the surface while causing relative motion between the energy source and the article surface and maintaining the flowing gas cover over the portion of the surface area which is being melted, so that a shallow surface layer will be melted, without significant heating below the melted layer, with the time of exposure of a point on the surface to the energy being less than about 0.1 sec,

e. allowing the melted layer to cool by conduction into the unmelted substrate, at a rate sufficient to cause the formation of a fine microstructure surface layer wherein at least one of the average surface layer crystal dimensions is less than about 1,000 Å.

9. A method according to claim 8 wherein the transition metal is chosen from the group consisting of Fe,Ni, and Co and mixtures thereof.

10. A method according to claim 8 or claim 9 wherein the metalloid is chosen from the group consisting of C,B and P and mixtures thereof.

11. A method according to any one of claims 8 to 10 wherein the energy source is a continuous laser.

12. A method according to any one of claims 8 to 11 wherein the energy source produces an electron beam.

13. A method according to any one of claims 8 to 12 wherein the gas flows at a rate in excess of about 2 feet per minute. (0.60 m/min).

14. A method according to any one of claims 8 to 13 wherein the thickness of the surface layer is less than about 50 mils (1270 μ).

15. A method according to any one of claims 8 to 14 wherein the cooling rate is in excess of about 10^4°F/sec (5.5 10^3°C/sec.).

16. A method for producing an amorphous surface layer on a metallic article as hereinbefore described with reference to the accompanying drawings.

Agents for the Applicants
ARTHUR R. DAVIES
Chartered Patent Agents
27, Imperial Square
Cheltenham
- and -
115, High Holborn
London W.C.1.

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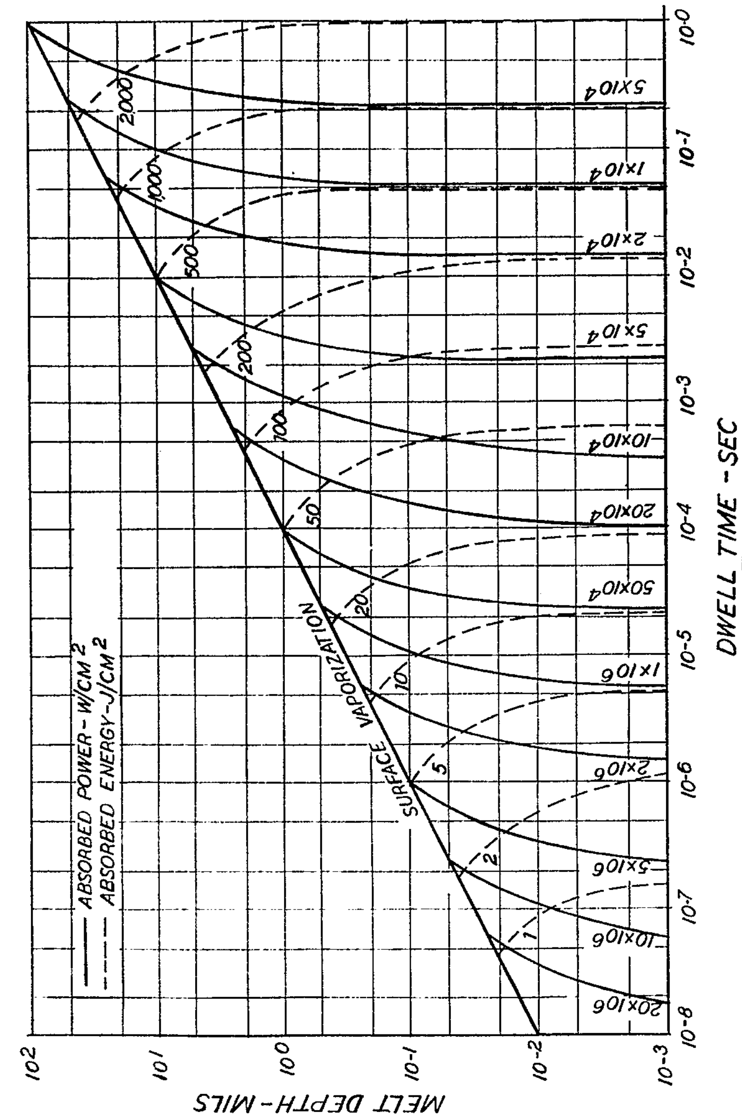
ABSORBED POWER - W/CM 2
ABSORBED ENERGY-J/CM 2
SURFACE VAPORIZATION
5x10 4
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2x10 4
5x10 4
10x10 4
20x10 4
50x10 4
1x10 6
2x10 6
5x10 6
10x10 6
20x10 6
2000
1000
500
200
100
50
20
10
5
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1
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10 -2
10 -3
10 -4
10 -5
10 -6
10 -7
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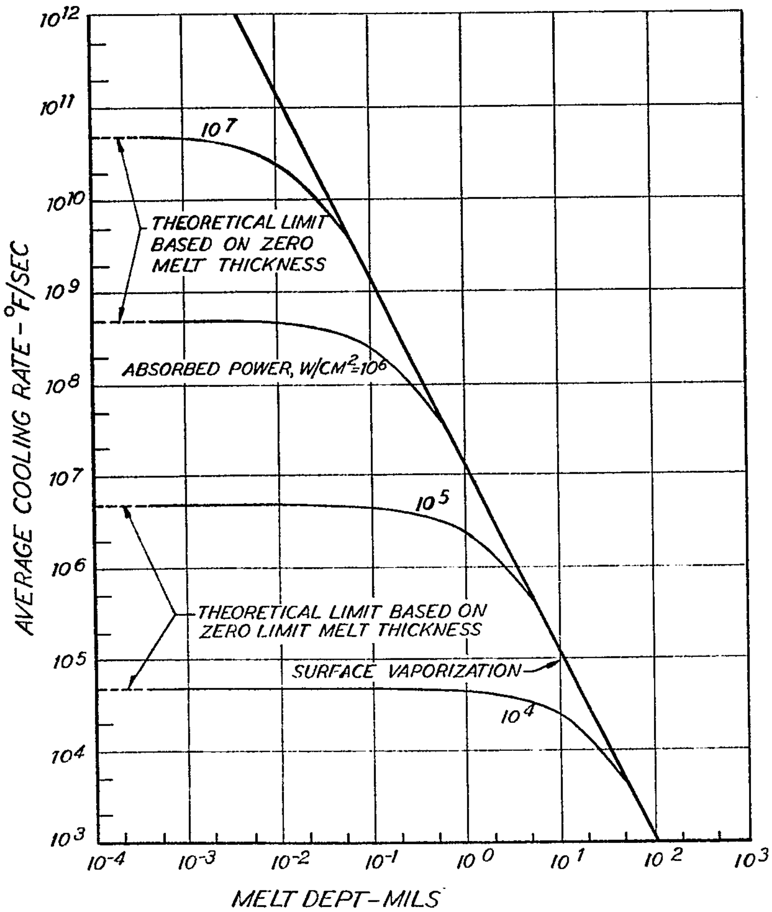
10 -3
DWELL TIME - SEC
MELT DEPTH - MILS

FIG. 1


10^12
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10^10
10^9
10^8
10^7
10^6
10^5
10^4
10^3
AVERAGE COOLING RATE - °F/SEC
10 7
THEORETICAL LIMIT BASED ON ZERO MELT THICKNESS
ABSORBED POWER, W/CM²=10⁶
10 5
THEORETICAL LIMIT BASED ON ZERO LIMIT MELT THICKNESS
SURFACE VAPORIZATION
10 4
10^-4
10^-3
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10 2
10^3
MELT DEPT-MILS

FIG. 2

FIG.3 (7.5X)

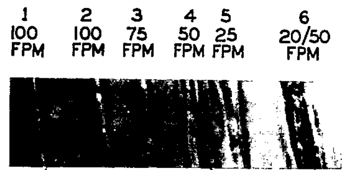

FIG.4 150X

FIG.5 (100 X)

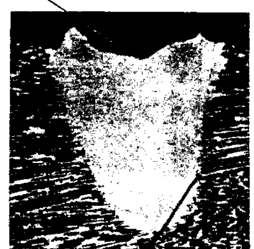

FIG.6 (1,000X)

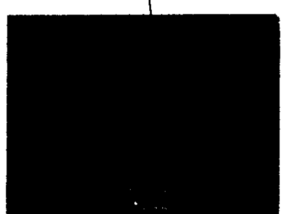

FIG.7 (1,000X

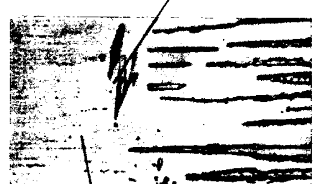

FIG.8 (33,000 X)

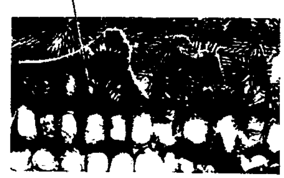

FIG.9 (13,000 X)