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EUROPEAN PATENT APPLICATION

⑳ Application number: 82630022.0

⑤① Int. Cl.³: **B 22 F 3/14**
B 22 F 3/24, C 22 C 1/05

㉔ Date of filing: 22.03.82

③① Priority: 24.03.81 US 247028

④③ Date of publication of application:
06.10.82 Bulletin 82/40

⑧④ Designated Contracting States:
CH DE FR GB IT LI NL SE

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⑤④ Sintering cycle including a low pressure hot isostatic pressing step.

⑤⑦ According to the invention a material made from powders and of the liquid phase sintering type is first vacuum sintered to substantially full density, except for the presence of occasional closed clean flaws, and then, without lowering the temperature below the solidus, is subjected to gas pressure of 100-1000psi for 15-60 minutes for the purpose of healing the flaws.

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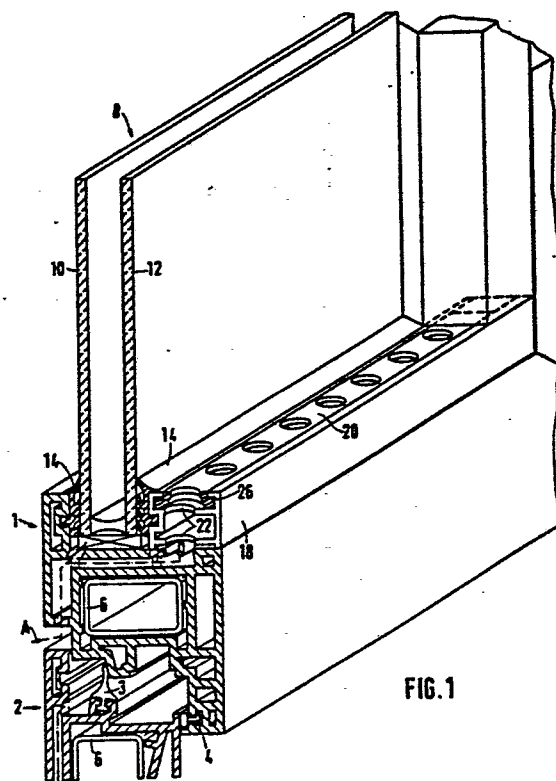


FIG. 1

SINTERING CYCLE INCLUDING A LOW PRESSURE HOT
ISOSTATIC PRESSING STEP.

This invention relates to a method of sintering a material from powder and of the liquid phase sintering
5 type, e.g., a mixture of tungsten carbide powder and cobalt powder, the resulting material being commonly referred to as cemented tungsten carbide.

It is well known in the art that the physical properties such as surface integrity and strength of some materials, such as cemented tungsten carbide, which have
10 already been vacuum sintered to substantially 100% of theoretical density may be significantly improved by subjecting the material to a hot isostatic pressing or "HIP" treatment. In the case of cemented tungsten carbide,
15 this step typically involves reheating an article of sintered cemented tungsten carbide to around 1350°C and then subjecting the material to isostatic pressure on the order of several thousand pounds per square inch for a period consuming several hours of cycle time. The primary
20 beneficial effects of such a HIP treatment is to reduce or eliminate any small pores which may remain after sintering, and, more significantly, to reduce or eliminate any larger randomly spaced holes, slits or fissures which may be present in the sintered cemented tungsten
25 carbide articles.

While HIP treatment as outlined above has been widely adopted in the manufacture of articles which must have the small pores and larger flaws reduced or eliminated after sintering, the methods and apparatus in common use
30 suffer from serious disadvantages. First, the pressures and temperatures typically involved, coupled with the long cycle times, dictate large and expensive apparatus to both generate and withstand the extreme conditions. Moreover, the demands placed on the apparatus, especially
35 the gas seals and the pumping equipment, often lead to failures. The considerations of the physical capabilities and integrity of the apparatus become even more significant as the size of the article to be treated increases. Furthermore, the sheer mass of the furnace, as dictated

by the physical strength required to withstand the pressures at operating temperatures, results in relatively long stabilization times, which even further tax the equipment and increase the overall cost of the treatment. And to the extent the articles must be transferred from the site of the sintering to another location for the HIP treatment, scheduling and transit considerations may serve to further increase the effective cost of the operations.

Finally, there is some evidence that the extended holding times at the typical HIP temperature and pressure may result in undesirable localized grain growth. Ironically, the large grains which may result, when localized in patches, can have deleterious effects very similar to the flaws which the HIP treatment is intended to reduce or eliminate.

An object of the present invention is the achievement of many of the benefits of a conventional HIP treatment through a process which avoids the use of the high operating pressures and long cycle times typically associated therewith.

Another object of the present invention is to provide an overall more efficient method for sintering and hot isostatic pressing articles.

A collateral object of the present invention is to provide a method for healing occasional closed clean flaws in sintered articles which avoids conditions which may lead to undesirable grain growth.

In a more specific application, an object of the present invention is to provide a method for producing articles formed of tungsten carbide and cobalt powders in which closed clean flaws are removed without resort to a conventional high pressure HIP treatment separate from and following conventional sintering.

Other objects and advantages will become apparent from the following description with reference to the accompanying drawings in which:

Fig. 1 is a photomicrograph at 75x magnification

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of a cross section of a cemented tungsten carbide bar made by conventional vacuum sintering from Carboloy[®] 100 (90% WC-10% Co by weight) powder and having a large
5 closed clean flaw;

Fig. 2 is a photomicrograph at 75x magnification of a cross section of a cemented tungsten carbide bar made in accordance with the present invention from Carboloy[®] 100 powder and showing a healed large closed clean flaw
-10 such as the flaw shown in Fig. 1;

Fig. 3 is a photomicrograph at 300x magnification of the same cross section as shown in Fig. 2;

Fig. 4 is a photomicrograph at 1500x magnification of the same cross section shown in Fig. 2;

15 Fig. 5 is a photomicrograph at 75x magnification of a cross section of a cemented tungsten carbide bar made by conventional vacuum sintering from Carboloy[®] 55A (87% WC-13% Co by weight) powder and having a large closed clean flaw;

20 Fig. 6 is a photomicrograph at 75x magnification of a cross section of a cemented tungsten carbide bar made in accordance with the present invention from Carboloy[®] 55A powder and showing a healed large closed clean flaw, such as the flaw shown in Fig. 5;

25 Fig. 7 is photomicrograph at 300x magnification of the same cross section shown in Fig. 6;

Fig. 8 is a photomicrograph at 1500x magnification of the same cross section shown in Fig. 6;

Fig. 9 is a photomicrograph at 75x magnification of
30 a cross section of a cemented tungsten carbide bar made in accordance with the present invention from Carboloy[®] 100 powder and showing a healed large closed clean flaw, such as the flaw shown in Fig. 1;

Fig. 10 is a photomicrograph at 300x magnification
35 of the same cross section shown in Fig. 9; and

Fig. 11 is a photomicrograph at 1500x magnification of the same cross section shown in Fig. 9.

While it is believed that the process according to the invention has utility in the treatment of a variety

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of materials made from powders and of the liquid phase sintering type, the invention is described below in the particularly advantageous application of the process to
5 cemented tungsten carbide.

In conventional production of cemented tungsten carbide articles, tungsten carbide powder and cobalt powder are mixed, poured into a mold and mechanically pressed to consolidate the powder mixture into a bri-
10 quette having the form of the mold. Depending on the application for the finished cemented tungsten carbide material, the cobalt content ranges up to about 25% by weight of the mixture. The pressed briquette is then sintered in vacuum or in a protective gas atmosphere. The
15 sintering cycle involves peak temperatures of 1350°C to 1450°C , depending on the alloy composition, and times at peak temperature of an hour or more. Typically the powders contain a wax to improve their initial compacted integrity, sometimes referred to as "green strength".
20 This wax may be driven off as a separate dewaxing operation at elevated temperatures (approximately 500°C) in a hydrogen atmosphere prior to sintering or in the sintering furnace as an initial, intermediate temperature step before application of the full sintering tempera-
25 ture.

During sintering a liquid phase forms, consisting of a solution of the carbide in cobalt, and densification of the body follows. On cooling the carbide precipitates from solution in the cobalt, and in the case of
30 tungsten carbide and cobalt alloys, the final fully dense structure consists of tungsten carbide in essentially pure cobalt. If the sintering temperature is too high undesirable coarsening of the structure may occur and if it is too low "under-sintering" occurs, evidenced by
35 excessive porosity.

Even is carefully controlled liquid phase sintering processes, the resulting cemented tungsten carbide material may still have a small degree of porosity which is undesirable.

The porosity that remains can be characterized either as small evenly distributed pores ranging up to about 25 microns in major dimension or as large randomly spaced holes, slits or fissures as large as 0.25mm as to 2.5mm in major dimension. The large flaws (sometimes hereinafter referred to as large closed clean flaws) consisting of large, randomly spaced holes, slits and fissures have the most serious adverse effects on surface integrity and strength because of their size and random distribution. It is to the elimination or reduction of these large flaws that the present invention is primarily addressed.

The present invention provides a process which eliminates the necessity of resorting to the high pressures and long cycle times encountered in conventional HIP treatment in order to heal the randomly spaced closed clean flaws which may remain after conventional vacuum sintering. While the theoretical mechanism is not precisely known, the applicant has observed that a cemented tungsten carbide body appears to exhibit lower strength at sintering temperature during initial sintering than it does when cooled and subsequently heated to the same temperature. The material could be said to have taken a "set" during cooling from the initial sintering temperature. The "structure" of the body at temperature during initial sintering is thought to be unique to that condition such that the application of relatively minor gas pressure after initial sintering has progressed, and before cooling the body to the solid state, results in successful closure of large flaws.

In any event, it has been found that the large flaws can be successfully healed as an adjunct to the initial sintering cycle by subjecting the tungsten carbide and cobalt material to gas pressure of 100-1000 psi for 15-60 minutes after vacuum sintering has been completed but without lowering the temperature of the material below the solidus.

While conventional vacuum sintering furnaces may not

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be, and are more than likely not, capable of withstanding pressurization above a few pounds per square inch, certain furnaces used in the ceramic sintering art are available which will withstand both vacuum and low pressure. Such a furnace is Model 45-8x12-G-G-EKO-6-A-22 made by Centorr Associates, Inc. which was used in the examples below.

The following examples show how to process of the present invention may be carried out to heal large closed clean flaws in a cemented tungsten carbide bar 1" X 1/4" X 1/4" in size.

Example 1 - Conventional vacuum sintering to show a large flaw- Carboloy® 100 powder

1. Material - Carboloy® 100 (90% WC- 10%Co) standard paraffinized powders.
2. Fill 16 gram mold with 8 grams of powder.
3. Place extruded paraffin rod - - 1/4 " long, .005" - .025" diameter -- on powder to produce large flaw.
4. Add remaining 8 grams of powder.
5. Press powder mechanically at 30,000 psi.
6. Dewax bar in H₂ atmosphere at 500°C.
7. Sintering Cycle - Vacuum only.

Temperature - 1350 - 1400°C.

Pressure - .1 - .3 mm of Hg ($1.3-3.9 \times 10^{-4}$ atmospheres)

Time - 90 minutes , then cool

The resulting cemented tungsten carbide bar from Example 1 has a large flaw shown in Fig. 1.

Example 2 - Process of present invention showing healing of large flaw- Carboloy® 100 powder.

1. Repeat steps 1-6 of Example 1.
2. Sintering Cycle:

a. Vacuum phase

Temperature - 1350 - 1400° C
Pressure - .1- .3 mm of Hg
Time - 60 minutes

b. HIP phase (follows vacuum phase directly)

Temperature - Maintain at 1350 - 1400°C.

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Pressure - 300 psi argon

Time - 30 minutes

The resulting cemented tungsten carbide bar from Example
 5 2 has a healed flaw shown in Figs. 2. (75X), 3 (300X)
 and 4 (1500X).

Example 3 - Conventional vacuum sintering to show large
 flaw - Carboloy[®] 55A powder.

1. Material - Carboloy[®] 55A (84%WC - 16%Co) standard
 10 paraffinized powders.
2. Fill 16 gram mold with 8 grams of powder.
3. Place extruded paraffin rod -- 1/4" long, .005" -
 .025" diameter -- on powder to produce large flaw.
4. Add remaining 8 grams of powder.
- 15 5. Press powder mechanically at 30,000psi.
6. Dewax bar in H₂ atmosphere at 500°C.
7. Sintering Cycle- Vacuum only
 - Temperature - 1350-1400°C
 - Pressure - .1-.3 mm of
 20 Hg ($1.3-3.9 \times 10^{-4}$ atmospheres)
 - Time - 90 minutes, then cool

The resulting cemented tungsten carbide bar from Example
 3 has a large flaw shown in Fig. 5.

Example 4 - Process of present invention showing hea-
 25 ling of large flaw - Carboloy[®] 55A powder.

1. Repeat steps 1 - 6 of Example 3.
2. Sintering Cycle:
 - a. Vacuum phase
 - Temperature - 1350 - 1400°C
 - 30 Pressure - .1-.3mm of Hg
 - Time - 60 minutes
 - b. HIP phase (follows vacuum phase directly)
 - Temperature - Maintain at 1350-1400°C
 - Pressure - 300 psi argon
 - 35 Time - 30 minutes

The resulting cemented tungsten carbide bar from Example
 4 has a healed flaw shown in Figs. 6 (75X), 7 (300X)
 and 8 ((1500X).

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Example 5 - Process of present invention showing healing of large flaw - Carboloy[®] 100 powder.

1. Repeat steps 1 - 6 of Example 1.
- 5 2. Sintering Cycle:
 - a. Vacuum phase
 - Temperature - 1350-1400°C
 - Pressure - .1 - .3mm of Hg
 - Time - 60 minutes
 - 10 b. HIP phase (follows vacuum phase directly)
 - Temperature - Maintain at 1350-1400°C
 - Pressure - 100 psi argon
 - Time - 30 minutes

The resulting cemented tungsten carbide bar from Example 15 5 has a healed flaw shown in Figs. 9. (75X), 10(300X) and 11 (1500X).

From the foregoing examples one can see that the disclosed method of liquid phase sintering including low pressure HIP treatment for healing large flaws in 20 cemented tungsten carbide can be successfully carried out at moderate pressures of 100 to 300 psi. Other tests have been conducted which show no discernable effect at 25 psi. Tests using pressures as high as 1000 psi, still a small fraction of the pressures typically employed in 25 conventional HIP treatment, have given excellent results. Accordingly, HIP pressures of between about 100 and 1000 psi have been found to be useful in closing flaws while when applied as a follow-on to a normal vacuum sintering cycle.

30 Considering the time period during which the low pressure HIP step according to the invention is applied, it is noted that the examples above employed 30 minutes of pressure application following vacuum sintering. Other tests in which the time period for application of the 35 pressure ranged between 15 and 60 minutes have also been conducted with successful results.

It is contemplated that, within the ranges set out above, i.e., 100 to 1000 psi and 15 to 60 minutes, for the application of pressure, those skilled in the art can

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readily arrive at suitable minimum pressures and application times to achieve the desired results for specific applications. It is recognized that somewhat higher
5 pressures and application times might also be employed while still avoiding the disadvantages attendant conventional high pressure HIP treatment. Given the obvious disadvantages of unnecessarily high pressures and/or unnecessarily long cycle times, however, it will be appreciated that the maximum benefits from the present invention may be achieved through achieving a suitable overall minimum balance between the two parameters which still yields the desired result.

Considering the matter of cycle times further, it
15 has been found that, because of the use of a low pressure HIP treatment step immediately following the vacuum sintering step, the latter can be shortened significantly so that the whole process -- including the low pressure HIP treatment -- can be of the same or only slightly
20 longer duration than conventional vacuum sintering alone. The reason for this surprising result is that low pressure HIP can begin as soon as the flaws and pores have been adequately sealed during vacuum sintering to prevent the entry of gas into the material, with the application
25 of pressure speeding the final consolidation. By contrast, in conventional vacuum sintering full consolidation under vacuum can only be achieved by continuing the sintering cycle beyond the point in time when the material is capable of withstanding the application of pressure
30 without the entry of gas into the material.

It has further been observed that articles treated by the sintering/low pressure HIP method according to the present invention appear to be free of the localized patches of coarse grains sometimes observed in articles
35 made from the same starting materials only treated by conventional, separate, vacuum sintering and high pressure HIP operations. Freedom from this localized coarse grain structure is viewed as a significant advantage in terms of the strength of the article inasmuch as such

- 10 -

grain structure can have deleterious effects very similar to the randomly oriented flaws sought to be reduced or eliminated by the HIP treatment. It is believed that
5 the avoidance of the extended holding times at the typical HIP temperature and pressure may account for the more desirable grain structure observed in articles treated according to the present invention.

In the practice of the invention in order to maintain the furnace temperature while switching from vacuum
10 sintering to low pressure HIP, it may be necessary to preheat the argon gas (or other gas) before it is introduced into the furnace to avoid temporarily depressing the temperature of the article sufficiently to cause
15 the "set" discussed above. It is noted that because of the relatively low pressures used, the pressurization can be accomplished by using compressed gas which is normally supplied in cylinders at around 2000 psi. Thus expensive pumping equipment may be eliminated.

20 Finally, while the process is especially useful in the manufacture of cemented tungsten carbide material, the process is considered to have application, to all materials made from powder by liquid phase sintering and may aid the densification of some materials sintered in
25 the solid state as well.

CLAIMS

1. A method for sintering a material from powders and of the liquid phase sintering type comprising:
 - 5 a) sintering the powders at a temperature above the solidus in a vacuum,
 - b) maintaining the temperature of the material above the solidus while applying an isostatic pressure of between 100 and 1000 psi with an
10 inert gas; and
 - c) maintaining the isostatic pressure of between 100 and 1000 psi for at least 15 minutes.
2. The method of claim 1, wherein the inert gas is preheated.
- 15 3. A method for healing large closed clean flaws in a material made from powders by liquid phase sintering in a vacuum at a temperature above the solidus comprising:
 - a) maintaining the temperature of the material
20 above the solidus after sintering while applying an isostatic pressure of between 100 and 1000 psi with an inter gas, and
 - b) maintaining the isostatic pressure of between 100 and 1000 psi for at least 15 minutes.
- 25 4. The method of claim 3, wherein the pressurized inert gas is preheated.
5. A method for sintering cemented tungsten carbide comprising:
 - a) sintering cobalt and tungsten carbide powders at
30 a temperature above the solidus in a vacuum,
 - b) maintaining the temperature of the material above the solidus while applying an isostatic pressure of between 100 and 1000 psi with an inert gas, and
 - c) maintaining the isostatic pressure of between
35 100 and 1000 psi for at least 15 minutes.
6. The method of claim 5, wherein the inert gas is preheated.
7. A method for healing large closed clean flaws in sintered cemented tungsten carbide by liquid phase sinter

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ring in a vacuum at a temperature above the solidus comprising:

5 a) maintaining the temperature of the material above the solidus after sintering while applying an isostatic pressure of between 100 and 1000 psi with an inert gas, and

b) maintaining the isostatic pressure of between 100 and 1000 psi for at least 15 minutes.

10 8. The method of claim 7, wherein the pressurized inert gas is preheated.

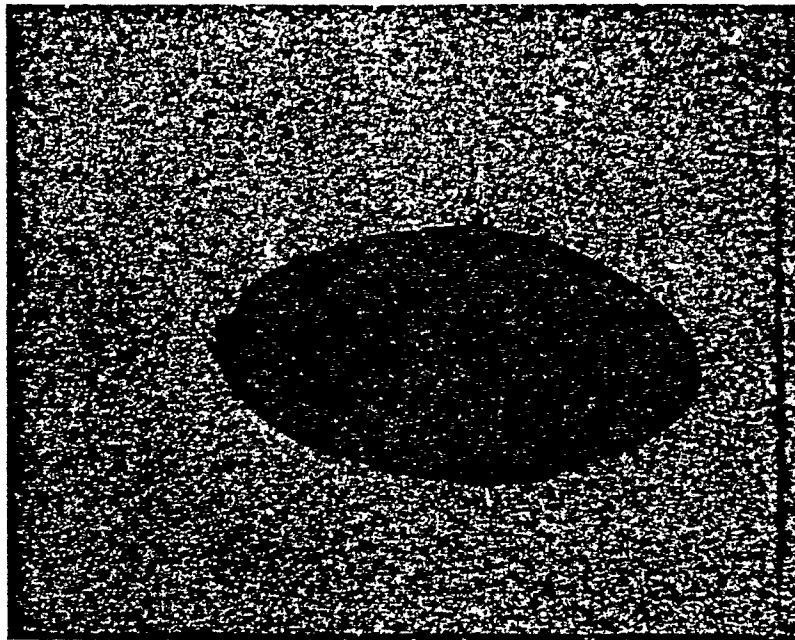
9. An article made from powders by liquid phase sintering in accordance with claim 1.

15 10. A cemented tungsten carbide article made in accordance with claim 5.--

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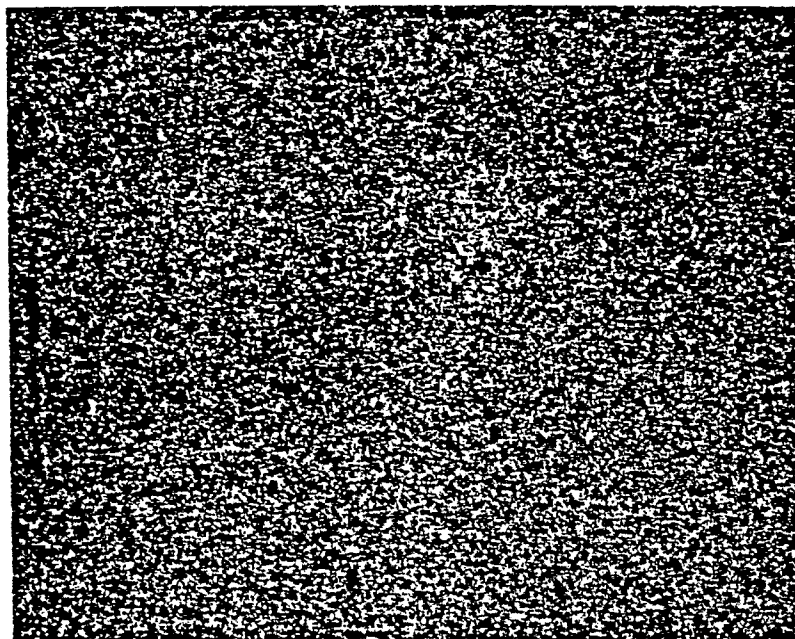
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V5301

FIG. 1

75X



V5362

FIG. 2

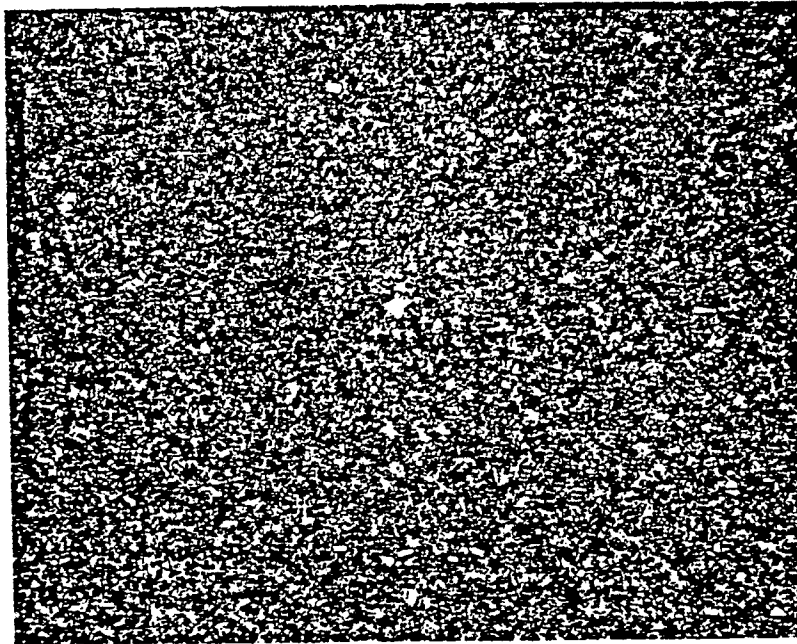
75X

1940

1940

0061988

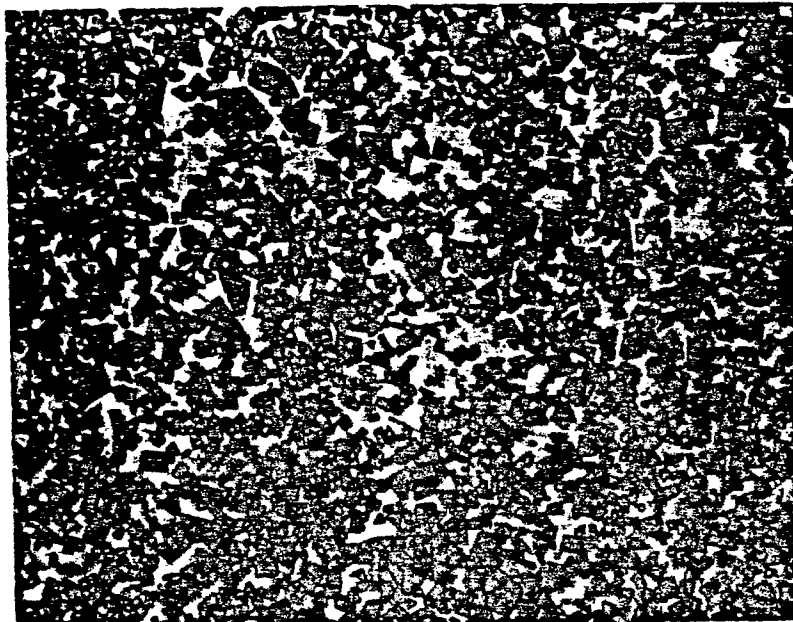
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V5362

FIG. 3

300X



V5362

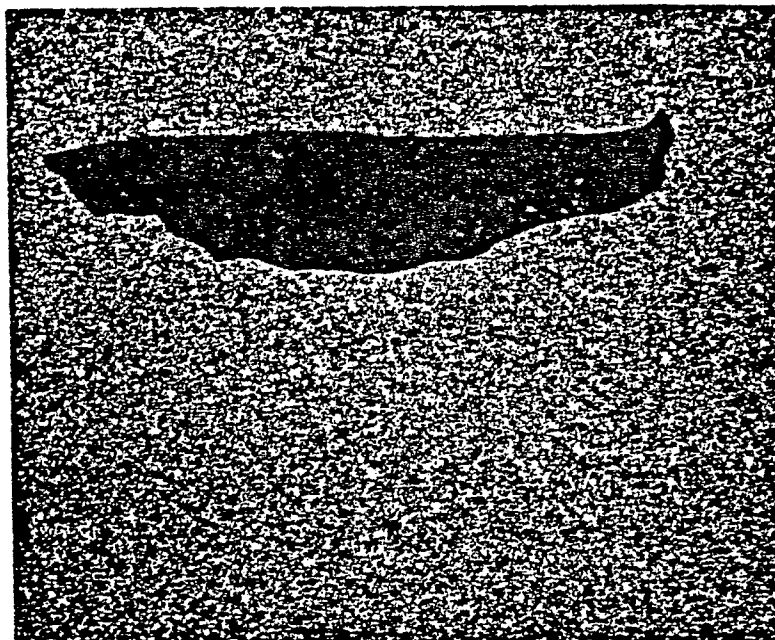
FIG. 4

1500X

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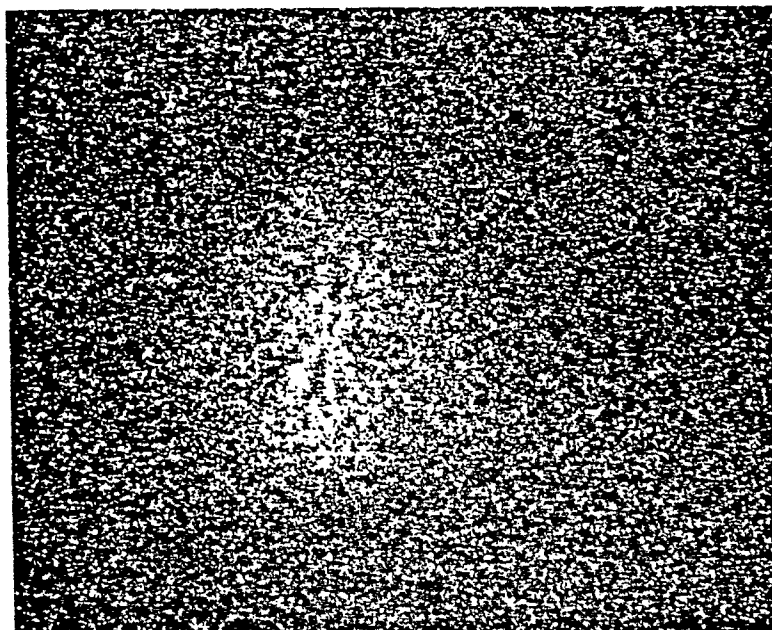
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L4371

FIG. 5

75X



V5377

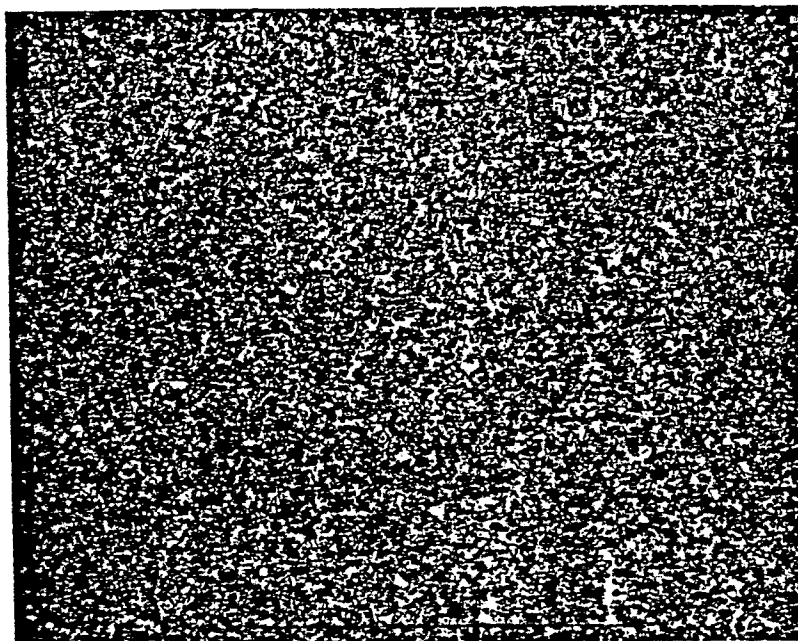
FIG. 6

75X

190

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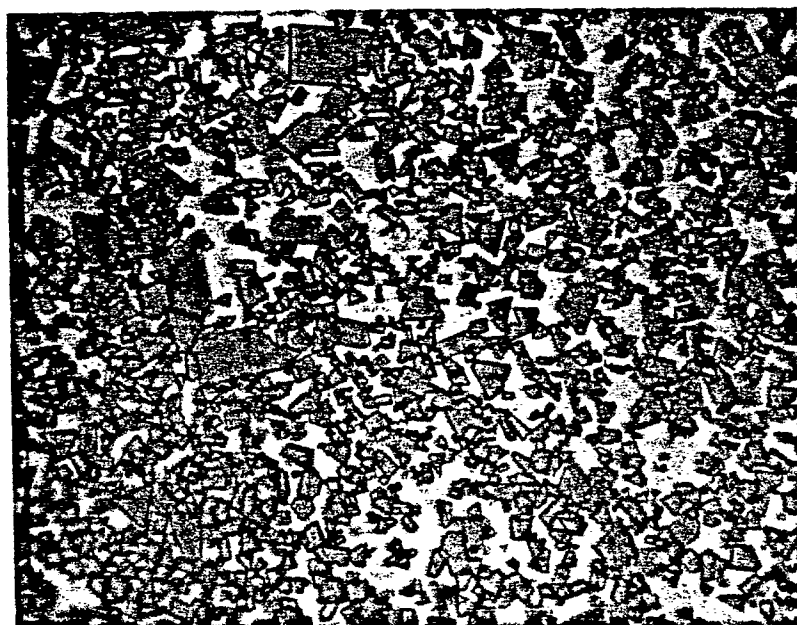
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V5377

FIG. 7

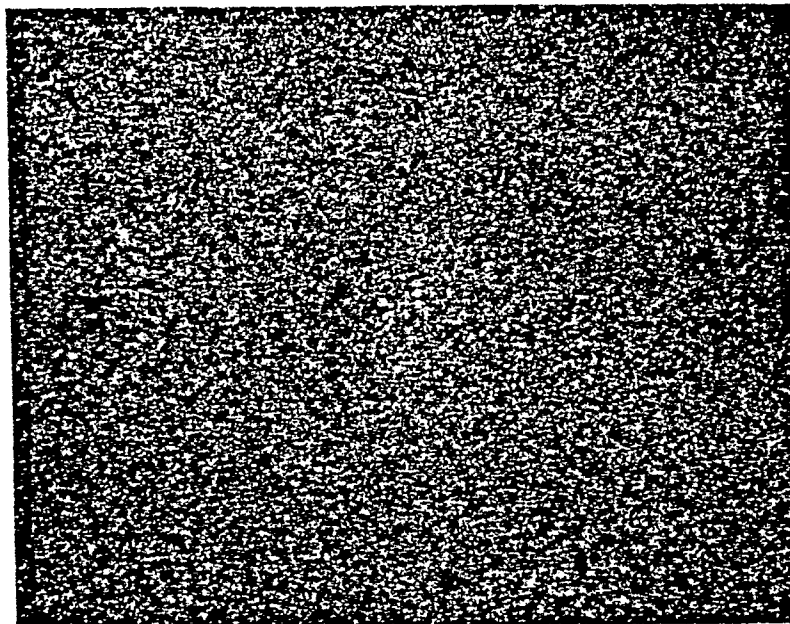
300X



V5377

FIG. 8

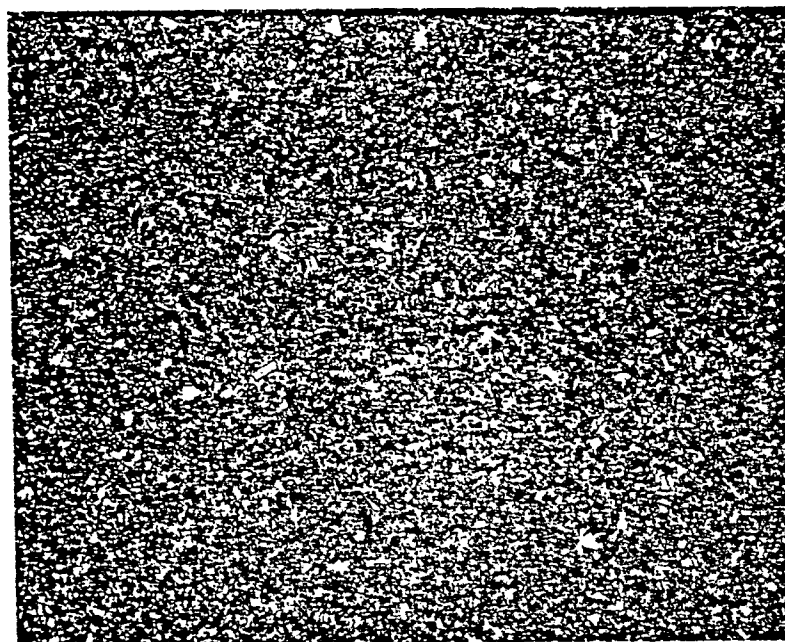
1500X



V5360

FIG. 9

75X



V5360

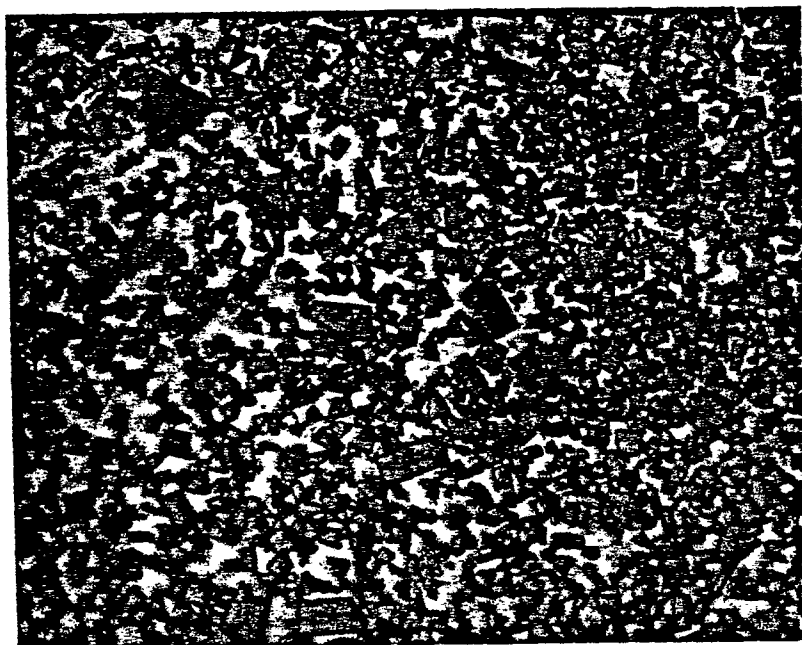
FIG. 10

300X

19.01

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V5360

FIG. 11

1500X



European Patent
Office

EUROPEAN SEARCH REPORT

0061988
Application number

EP 82 63 0022

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 2)
X	US-A-3 469 976 (R.K.ILER) *Column 5, line 55 - column 8, line 5; claim 21*	1-10	B 22 F 3/14 B 22 F 3/24 C 22 C 1/05
X	GB-A-1 300 864 (ASEA) *Page 1, line 52 - page 2, line 59; claims 4,6*	1-10	
A	FR-A-2 288 585 (HOWMET CORP.) *Claim 1*	3	
A	FR-A-2 387 720 (KRUPP)		
			TECHNICAL FIELDS SEARCHED (Int. Cl. 2)
			B 22 F
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 02-07-1982	Examiner SCHRUERS H.J.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	