The invention relates to a diffusion alloyed iron powder wherein tungsten W is bonded to the surfaces of the particles of an iron or iron-based powder, the diffusion alloyed iron powder comprises by weight-%: 30-60 W, balance essentially only iron and unavoidable impurities.
A DIFFUSION ALLOYED IRON POWDER

TECHNICAL FIELD

The invention relates to a metal powder suitable for producing lead free bullets, in particular bullets having a density of approximately 8-15 g/cm³.

BACKGROUND

The poisoning effect of lead contamination on the environment with emphasis on soil and water has been in focus during the last decades. In many countries certain ammunition containing lead has been prohibited.

Due to a number of factors such as availability, price and material properties lead has been the dominating material for bullet and shot shell manufacturing. The density of lead at room temperature is 11.35 g/cm³ which is comparably high in relation to many other materials. The high density enables lead-based projectiles to maintain a higher kinetic energy and more accurate flight pattern over long distances than less dense materials.

Further, since lead projectiles have dominated the market, it would be an advantage if an alternative bullet has a similar density as lead projectiles minimising differences in long range trajectories and in firearm recoil. Thereby the shooter knows where to aim and the recoil consistent with that of shooting a lead projectile so the "feel" of shooting is the same as that of shooting a lead bullet.

Further, with reference to hunting bullets, a major demand is also that the bullet shall expand and cause fatal damage when penetrating the game. This condition is fulfilled with lead since this element is very ductile and has high degree of deformability.

However, for certain applications as e.g. bird hunting, one would like to minimise the expansion of the bullet and therefore full metal jacket bullets are commonly used. For sport shooting accuracy is important and the deformability of the bullets is not necessary for this kind of bullet.

Therefore it is desirable to provide a more environmental friendly bullet which has a similar density as lead. However alternative elements with high density are scarce, and for the moment only tungsten (W) and bismuth (Bi) are used commercially for
production of lead free ammunition with high density. Tungsten has a density of 19.8 g/cm$^3$ and the toxic effects of tungsten is considered to be comparably limited. Further it would be advantageous if the costs of such bullets can be kept low. The price for tungsten is very dependent on the particle size and purity and very expensive atomised powders are available on the market. However, tungsten oxide (W03) which is an intermediate product in the production of W, is comparably cheap.

US 5,527,376 claims a shot pellet or small arms projectile comprising 40% by weight to 60% by weight tungsten and from 60% by weight to 40% by weight iron prepared by sintering tungsten containing powders having median particle sizes below about 6 microns at a temperature sufficient to form a material consisting primarily of an intermetallic compound of tungsten and iron, a projectile comprising 40-60 wt% W and 60-40 wt% Fe, formed by sintering tungsten containing powder.

US 5,950,064 presents a method for the manufacture of lead-free shots with a density equal to or higher than lead. Ferrotungsten (typically 70%-80%, by weight, tungsten and the balance iron) and other iron-tungsten alloys are most preferred due to a relatively low cost when compared to tungsten metals and other tungsten base alloys.

US 5,399,187 shows a lead free bullet, comprising: a compacted composite containing a high-density first constituent selected from the group consisting of tungsten, tungsten carbide, ferrotungsten and mixtures thereof; and a lower density second constituent selected from the group consisting of tin, zinc, aluminium, iron, copper, bismuth and mixtures thereof.

US 6,823,798 describes manufacturing processes for articles that are formed from compositions of matter that include powders containing tungsten and at least one binder.

US 6,112,669 describes a lead-free projectile made from a composition containing about 5-25% by weight tungsten and more than about 97% by weight tungsten plus iron.

US 6,527,880 describes a non-toxic shot having a composition of 20-70% W, 10-70% Ni and 0-55% Fe.

US 6,640,724 describes a method for manufacturing a frangible projectile from a mixture of powders having a composition that consists essentially of up to 35% ferrotungsten, up to 3% lubricant, and the balance iron. The mixture is compacted at a
pressure of between about 138 MPa and about 827 MPa to form a compact. The compact is optionally sintered at a temperature no greater than about 900°C.

OBJECT OF THE INVENTION

One object of the invention is to provide an iron-based powder and a powder composition which is suitable for manufacturing lead free ammunition. A further objective is to provide a non-toxic projectile manufactured from said iron-based powder.

Several further objectives of the present invention, which may be achieved individually or in groups according to various aspects of the present invention, are:
- that the projectile can be made to have a density in the range of approximately 8\textsuperscript{-15} g/cm\textsuperscript{3}, preferably in the range of approximately 10-13 g/cm\textsuperscript{3}, more preferably in the range of approximately 10.5-12 g/cm\textsuperscript{3}, and even more preferably a density of approximately 11.3-11.8 g/cm\textsuperscript{3};
- that the projectile material is non-toxic or at least less toxic than lead to wildlife and the environment;
- that the projectile can be made magnetic for game-law purposes;
- that the projectile will less likely fracture or disintegrate upon target impact;
- that the projectile will less likely expand or deform upon target impact;
- that the projectile which, by virtue of ferromagnetic properties, may be readily salvaged for reuse;
- that the projectile can be manufactured at comparably low costs;
- that the iron based powder can be produced at comparably low costs; and
- that the alloying element(s) in the iron-based powder are evenly dispersed.

SUMMARY OF THE INVENTION

At least one of the above mentioned objects are solved by providing a diffusion alloyed iron powder having tungsten bonded to the surfaces of the powder particles, which diffusion alloyed iron powder comprises 30-60 wt% tungsten, balance essentially only iron and unavoidable impurities.

The diffusion alloyed powder of the invention has been shown to be suitable for producing lead free bullets, in particular when the diffusion alloyed powder is admixed with graphite in an amount of 1-4 wt% C.
Therefore a metallurgical powder composition is proposed, which composition comprises: at least 90 percent by weight of the diffusion alloyed iron powder of the invention and about 0.05 to about 2 percent by weight of a lubricant and optionally about 0.05 to about 2 percent by weight of a binder. Preferably the composition further comprises 1-4 wt% C in the form of Graphite.

Further a process for producing a diffusion alloyed iron powder which comprises: 30-60 wt% tungsten, balance essentially only iron and unavoidable impurities, said process comprises: a) mixing a tungsten oxide and an atomized iron powder, b) and annealing the mix of step a) under a reducing atmosphere whereby the tungsten oxide is reduced and tungsten is bonded to the surfaces of the iron powder particles of the iron powder.

Preferably in step b) of the process for producing the diffusion alloyed iron powder; the annealing is performed at a temperature of at least 800°C, more preferably at least 900°C and at a temperature below 1500°C, more preferably below 1200°C. The annealing is preferably performed during at least 30 minutes, more preferably at least 45 minutes.

Preferably in step b) of the process for producing the diffusion alloyed iron powder; the reduced atmosphere comprises essentially hydrogen.

Further a method for producing a bullet comprising:
   a) providing a powder metallurgical composition including 1) a lubricant, 2) a diffusion alloyed iron powder comprising 30-60 wt% W and at least 40 wt% Fe, and 3) 1-4 wt% C in the form of graphite,
   b) forming a green body from the powder metallurgical composition; and
   c) sintering the green body in a reducing or neutral atmosphere, at an atmospheric pressure or below, and at a temperature above 1100°C.

Preferably in step b) of the method for producing the bullet; the green body is formed by cold compaction of the mixture, where preferably the compaction pressure is within the range of 500-1500 MPa, more preferably at least 800 Mpa, and where preferably the temperature during compaction is below 100°C.

Alternatively in step b) of the method for producing the bullet; the green body is formed by warm compaction of the mixture, where preferably the compaction pressure is within
the range of 500-1500 MPa, preferably at least 800 Mpa, and where preferably the temperature during compaction is within the range of 100-200°C.

Preferably in step c) of the method for producing the bullet; the sintering temperature is in the range of 1100°C to 1400°C.

The sintered density of the bullet produced according to the bullet preferably has a density of at least 10 g/cm³, more preferably at least 11 g/cm³. Such bullets are suitable as shot gun bullets and hunting bullets.

The bullet may be coated with a jacket from the group consisting of tin, zinc, copper, brass and plastic.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a metallographic picture showing the sintered structure of a W/FE/C-alloy according to the present invention,

FIG. 2 is a metallographic picture showing the W-particles embedded in the Fe-C matrix of a W/FE/C alloy according to the present invention, and

FIG. 3 is a metallographic picture showing the sintered structure of a bullet manufactured from a diffusion alloyed powder of the invention.

EXPERIMENTAL PROCEDURE

Three diffusion alloyed iron powders - referred to, in the present application, as DA 1, DA 2 and DA 3 - were prepared. This was done by mixing 227 grams of WO3, from the company H.C. Starck, and 120 grams of different iron powders, iron powder 1, iron powder 2 and iron powder 3 - the numbering of the iron powders corresponding to the numbering of the diffusion alloyed iron powders. I.e. DA 1 was prepared from iron powder 1 and so on. The iron powders are shown in Table 1 and the diffusion alloyed powders are shown in Table 2.

The WO3-powder from H.C. Starck had the following properties: wt% WO3 =99,9, AD 4,8 g/cm³, d₉₀=29 µm and d₅₀=12 µm.
Table 1

<table>
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<tr>
<th>Powder</th>
<th>Chemical composition</th>
<th>D50</th>
<th>D90</th>
<th>Comments</th>
</tr>
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<tbody>
<tr>
<td>Iron powder 1</td>
<td>Fe &gt;99 wt%</td>
<td>34</td>
<td>45</td>
<td>Water atomised. annealed</td>
</tr>
<tr>
<td>Iron powder 2</td>
<td>Fe &gt;99 wt%</td>
<td>38</td>
<td>63</td>
<td>Sponge, non-annealed raw powder</td>
</tr>
<tr>
<td>Iron powder 3</td>
<td>Fe &gt;99 wt%</td>
<td>33</td>
<td>55</td>
<td>Water atomised, non-annealed raw powder</td>
</tr>
</tbody>
</table>

Respectively mix of iron powder 1, 2 and 3 and WO3 where heat treated in a continuous furnace during 60 minutes at a temperature of 1000°C, the atmosphere being 100% Hydrogen. During this heat treatment, the fine particles of the WO3 powder bonds to the coarser iron powder particles. After cooling the resulting soft cakes were milled, and approximately 300 grams of the diffusion alloyed powders, DA 1, 2 and 3, were obtained respectively. Chemical analysis showed that the resulting diffusion alloyed powders DA 1, 2 and 3 comprised 40 wt% Fe, 60 wt% W and inevitable impurities.

Table 2

<table>
<thead>
<tr>
<th>Powder</th>
<th>Base powder</th>
<th>W</th>
<th>Fe</th>
<th>D50</th>
<th>D90</th>
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<tbody>
<tr>
<td>DA 1</td>
<td>Iron powder 1</td>
<td>60 wt%</td>
<td>40 wt%</td>
<td>34</td>
<td>46</td>
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<tr>
<td>DA 2</td>
<td>Iron powder 2</td>
<td>60 wt%</td>
<td>40 wt%</td>
<td>36</td>
<td>64</td>
</tr>
<tr>
<td>DA 3</td>
<td>Iron powder 3</td>
<td>60 wt%</td>
<td>40 wt%</td>
<td>33</td>
<td>55</td>
</tr>
</tbody>
</table>

A number of compositions were tested. For each composition test samples were produced by filling a form (10mm diameter and 2mm thickness) with the powder metallurgical compositions shown in Table 3. These samples were then compacted at a compaction pressure of 1000 Mpa followed by sintering in a 100% Hydrogen atmosphere during 1 hour and at a temperature of 1325°C. For each composition the green density and sintered density was measured as averages from their corresponding test samples. The aim was to create some sort of liquid phase sintering and the additives FeSi, FeB, C and carbonyl nickel were evaluated as seen in Table 3.
As can be seen in Table 3 the best results were achieved for composition A, E and F - all being mixed with 2 wt% C in the form of Graphite (grade UF). The highest sintering density was achieved for composition A, however composition E and F closely followed.

These results clearly shows that an iron powder having tungsten bonded to the surfaces of the iron powder particles can be achieve a bullet density similar to lead bullets and would thus be a suitable alternative for producing lead free bullets - in particular when admixing graphite to the powder metallurgical composition in order to facilitate liquid phase sintering.

FIG. 1 and FIG. 2 show metallographic pictures for composition A. In FIG. 1 it can be seen that the porosity is more pronounced in the centre of the specimen and FIG. 2 shows how the W-particles are embedded in the Fe-C matrix.
It is obvious that by optimizing the production process the tungsten content could be further reduced - for a sintered density of 11.8 g/cm³ the theoretical tungsten content is approximately 30 wt%. Further, it is likely that by optimizing the process the sintering temperature may also be reduced, preferably below 1250°C while still maintaining liquid phase sintering.

Thus according to the present invention a projectile produced from the powder of the invention may have a density in the range of approximately 8-15 g/cm³, preferably in the range of approximately 10-13 g/cm³, more preferably in the range of approximately 10.5-12 g/cm³, and even more preferably a density of approximately 11.3-11.8 g/cm³. However, it should be understood that the projectile of the invention may have a density outside of these illustrative ranges and within further subsets of these ranges.

FIG. 3 shows metallographic pictures of a bullet produced from composition A of Table 3. The porosity reduces the tendency for ricochets as well as improves the adherence of the lubricant put on the surface.

Further, if the projectiles are jacketed, compacting could be done in the jacket and sintered therein. Alternatively, the projectiles could be compacted and sintered before being inserted into the jackets. If the projectiles are coated, they would be coated after compacting and sintering.
CLAIMS

1. Diffusion alloyed iron powder characterised in that tungsten W is bonded to the surfaces of the particles of an iron or iron-based powder, the diffusion alloyed iron powder comprises by weight-%:
   30-60 W,
   balance essentially only iron and unavoidable impurities.

2. A diffusion alloyed iron powder according to anyone of claim 1 wherein the iron or iron-based powder is a water atomised powder.

3. A diffusion alloyed iron powder according to anyone of claim 1 or 2 wherein the iron or iron-based powder is a sponge iron powder.

4. A metallurgical powder composition which comprises: at least 90 percent by weight of a diffusion alloyed iron powder and about 0.05 to about 2 percent by weight of a lubricant and optionally about 0.05 to about 2 percent by weight of a binder, the weights based on the total weight of the metallurgical powder composition characterised in that the diffusion alloyed iron powder is an iron or an iron-based powder having tungsten W bonded to the surfaces of the iron or iron-based powder particles, the diffusion alloyed iron powder comprises by weight-%:
   30-60 W,
   balance essentially only iron and unavoidable impurities.

5. Powder composition according to claim 4 wherein the composition comprises 1-4 wt% carbon C in the form of Graphite.

6. Process for producing a diffusion alloyed iron powder which comprises in weight-%:
   30-60 W
   balance essentially only iron and unavoidable impurities,
   said process comprises:
   a) mixing a tungsten oxide and an atomized iron powder, and
   b) annealing the mix of step a) under a reducing atmosphere whereby the tungsten oxide is reduced and tungsten is bonded to the surfaces of the iron powder particles of the iron powder.
7. Process according to claim 6 wherein in step b) the annealing is performed for at least 30 minutes, preferably at least 45 minutes.

8. Process according to anyone of claim 6 or 7 wherein in step b) the annealing is performed at a temperature of at least 800°C, preferably at least 900°C and at a temperature below 1500°C, preferably below 1200°C.

9. Process according to anyone of claim 6 to 8 wherein in step b) the reduced atmosphere comprises essentially hydrogen.

10. Method for producing a bullet comprising:
    a) providing a powder metallurgical composition including 1) a lubricant, 2) a diffusion alloyed iron powder comprising 30-60 wt% W and at least 40 wt% Fe, and 3) 1-4 wt% C in the form of graphite,
    b) forming a green body from the powder metallurgical composition; and
    c) sintering the green body in a reducing or neutral atmosphere, at an atmospheric pressure or below, and at a temperature above 1100°C.

11. Method according to anyone of claim 10 wherein in b) the green body is formed by cold compaction of the mixture, where preferably the compaction pressure is within the range of 500-1500 MPa, preferably at least 800 Mpa, and where preferably the temperature during compaction is below 100°C.

12. Method according to anyone of claim 10 wherein in b) the green body is formed by warm compaction of the mixture, where preferably the compaction pressure is within the range of 500-1500 MPa, preferably at least 800 Mpa, and where preferably the temperature during compaction is within the range of 100-200°C.

13. Method according to anyone of claim 10 to 12 wherein in c) the sintering temperature is in the range of 1100°C to 1400°C.

14. Powder metallurgically manufactured bullet, characterised in that the bullet comprises by weight-%: 30-60 W, 1-4 wt% C, balance essentially only iron and unavoidable impurities.
15. Bullet according to claim 14 wherein the sintered density of the bullet is at least 10 g/cm³, preferably at least 11 g/cm³.

16. Bullet according to anyone of claim 14 or 15 wherein the bullet is coated with a jacket selected from the group consisting of tin, zinc, copper, brass and plastic.

17. Bullet according to anyone of claim 14 or 15 wherein the bullet is a shotgun bullet.

18. Bullet according to anyone of claim 14 to 16 wherein the bullet is a hunting bullet.
Fig. 1

Fig. 2

Iron matrix  W-particle  Pore
Fig. 3
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

IPC: see extra sheet. According to International Patent Classification (IPC) or to both national classification and IPC.

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC: B22F, C22C, F42B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE, DK, FI, NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
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<td>US 4954171 A (TAKAJO ET AL), 4 Sept 1990 (04.09.1990), claim 6, abstract</td>
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<td>A</td>
<td>WO 2005102564 A1 (JFE STEEL CORPORATION), 3 November 2005 (03.11.2005), abstract</td>
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<td>DE 940712 C (HUSQVARNA VAPENFABRIKS AKTIEBOLAG), ZZ March 1956 (22.03.1956), see the whole document</td>
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<td>A</td>
<td>US 5527376 A (AMICK ET AL), 18 June 1996 (18.06.1996), claims 1-2, abstract</td>
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Further documents are listed in the continuation of Box C.

See patent family annex.

Date of the actual completion of the international search: 18 March 2008

Date of mailing of the international search report: 2008-03-20

Name and mailing address of the ISA/

Swedish Patent Office

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Facsimile No. +46 8 666 02 86

Authorized officer

Mats Raidla/Eo

Telephone No. +46 8 782 25 00

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B22F 1/00 (2006.01)
B22F 1/02 (2006.01)
C22C 33/02 (2006.01)
F42B 7/00 (2006.01)

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The password is LQONGUWUM.

Paper copies can be ordered at a cost of 50 SEK per copy from PRV InterPat (telephone number 08-782 28 85).

Cited literature, if any, will be enclosed in paper form.
### International Search Report

**Information on Patent Family Members**

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