



(51) International Patent Classification:

B22F 3/00 (2006.01) *C22B 34/36* (2006.01)
C22B 5/12 (2006.01) *C22C 35/00* (2006.01)

(21) International Application Number:

PCT/SE2014/050654

(22) International Filing Date:

27 May 2014 (27.05.2014)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

1300384-3 27 May 2013 (27.05.2013) SE

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(81) Designated States (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY,

BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

- with international search report (Art. 21(3))
- with amended claims (Art. 19(1))

(54) Title: IRON AND TUNGSTEN CONTAINING BRIQUETTES

(57) Abstract: The invention relates to iron and tungsten containing briquettes and a process for producing the briquettes. A green briquette is produced from mixing an iron powder, a tungsten containing powder, and briquetting the mixture.



WO 2014/193299 A1

IRON AND TUNGSTEN CONTAINING BRIQUETTES

TECHNICAL FIELD

The present invention relates to a process for producing iron and tungsten containing
5 briquettes. The invention also relates to briquettes produced by the process.

BACKGROUND

WO11053231 discloses a method for producing an iron- and tungsten containing
powder or powder agglomerate. A tungsten carbide containing powder is mixed with an
10 iron oxide powder and/or a tungsten oxide containing powder and optionally an iron
powder. The mix is heated in a neutral or weakly reduced atmosphere.

WO2008091210 discloses an iron a tungsten containing powder comprising 30-60 % by
weight of W and balance Iron. The powder is made by mixing an iron powder with a
15 WO₃-powder. A bullet can be produced from the powder.

OBJECTS OF THE INVENTION

It is an object of the invention provide a novel iron and tungsten containing material
suitable for tungsten addition in melting industries e.g. steel, foundry and superalloy
20 industry, and a process for producing such material in a comparably cost efficient
manner.

DESCRIPTION OF THE INVENTION

At least one of the above mentioned objects is at least to some extent achieved by a
25 process for producing an iron and tungsten containing briquettes including the steps of:

a) providing a mixture comprising (in weight-%):

- | | |
|------------|---|
| 1-40 | iron containing powder |
| 2-97 | tungsten containing powder containing at least one of |
| | tungsten oxides and tungsten carbides, |
| optionally | |
| 1-25 | carbon powder, |

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2-90 molybdenum containing powder

b) adding to the mixture:

a liquid, preferably water,

optionally one or more of:

5

binder,

slag former,

desulfurizer;

c) briquetting to provide a plurality of green briquettes

- 10 By this process it is possible to produce iron and tungsten containing green briquettes. The non-reduced green briquettes may be used as a substitute for traditionally manufactured ferrotungsten and/or ferromolybdenum alloys, when alloying the melt in industrial production. The green briquettes can be produced at lower costs than standard grades of ferroalloys. Their porous structure facilitates quick dissolving time in a steel melt. The briquettes can be easily transported on a conveying belt without the risk of rolling off.
- 15

When preparing the mixture the total amount of added water is around 1-10 % by weight the mixture, more preferably 2-5 % by weight.

20

Preferably neither binder nor slag former is used. The iron containing powder when mixed in wet condition strengthens the briquettes, making the use of a binder unnecessary. Thereby the amount of impurities can be reduced.

- 25 Optionally the method includes the step:

a) drying the green briquettes.

By drying the green briquettes, the risk of cracking due to quick vaporisation of the liquid, when heated at high temperatures, is minimised.

- 30 Preferably the optional drying step includes at least one of the following:

- drying the green briquettes to a moisture content less than 5 % by weight, preferably less than 3 % by weight;

- drying the green briquettes at a temperature in the range of 50-250 °C, preferably 80-200 °C, more preferably 100-150 °C.

When drying the briquettes there is a temperature increase even when no external heat is used. This is believed to be from reactions when the iron oxidises. The strength of the briquettes also increases. This makes it possible to provide sufficiently strong briquettes that without the need of adding binders, i.e. the iron powder replaces the need of a binder. Dust problems are also minimised.

Many different kinds of industrial dryers can be used. The briquettes may also be dried without active heating, e.g. in ambient air temperature. In a dryer vapour may be removed by a gas stream or by vacuum. For improved process economy, drying time in a dryer is preferably in the range of 10- 120 minutes, more preferably 20-60 minutes. But longer drying times are of course viable.

15

The moisture content is defined as water present in the green briquettes apart from water of crystallization. The moisture content can be determined by a LOD (loss on drying) analysis in accordance to ASTM D2216 – 10. Dry matter composition refers to the composition for a dried specimen, i.e. excluding any moisture present in the green briquettes.

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Preferably the method includes the step:

- b) reducing the green briquettes to provide a plurality of reduced briquettes.

Preferably the reduction step includes at least one of the following:

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- reducing at a temperature in the range of 800-1500 °C, preferably 1050-1400 °C, more preferably 1100-1300 °C, most preferably 1150-1250 °C;
- reducing during at least 20 minutes, more preferably at least 30 minutes.
- reducing in a furnace supplied with an inert or reducing gas, preferably supplied with a weakly reducing gas
- reducing at an operating pressure in the range of 0.1-5 atm, preferably 0.8-2 atm, more preferably 1.05-1.2 atm.

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-

By monitoring the formation of CO/CO₂ it can be determined when the reduction process is finished. The reduction time can be optimised by measuring the formation of CO and CO₂; in particular CO since CO₂ is mainly formed during the first minutes of reduction where after CO formation is dominating until the carbon source is consumed or all reducible oxides have been reduced. Preferably the reduction time is at most 10 hours, preferably at most 2 hours, more preferably at most 1 hour. Depending on the reduction time, the reduction temperature, and the relation between carbon and reducible oxides in the briquettes; the reducible oxides of the briquettes can be partially or fully reduced.

The atmosphere within the furnace is preferably controlled by supplying an inert or a reducing gas, preferably a weakly reducing gas, at one end of the furnace and evacuating gases (e.g. reaction gases (e.g. CO, CO₂, and H₂O) and the supplied gas) at the opposite end, more preferably, supplying the inert or reducing gas counter current at an outlet side of the furnace, and evacuating gases at an inlet side of the furnace. I.e. the inert or reducing gas is preferably supplied counter flow. The inert or a reducing gas may e.g. be argon, N₂, H₂, or any mixture of H₂/N₂ (e.g. 5:95 by vol.).

The reduction furnace is preferably a continuous furnace but may also be a batch furnace. In a continuous furnace the briquettes are conveyed from an inlet to and outlet during the reduction. Examples of furnaces are for example rotary kilns, rotary heart furnaces, shaft furnaces, grate kilns, travelling grate kilns, tunnel furnaces or batch furnaces. Other kinds of furnaces used in solid state direct reduction of metal oxides may also be employed. In a preferred embodiment a belt furnace is used.

Preferably the reduction furnace operates at pressure in the range of 0.1-5 atm, preferably 0.8-2 atm, more preferably at a pressure in the range of 1.0-1.5 atm, most preferably 1.05-1.2 atm.

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The atmosphere within the reduction furnace is preferably controlled by supplying an inert or a reducing gas, preferably a weakly reducing gas, at one end of the furnace and

evacuating gases (e.g. reaction gases (e.g. CO, CO₂, and H₂O) and the supplied gas) at the opposite end, more preferably, supplying the inert or reducing gas counter current at the outlet side of the furnace, and evacuating gases at the inlet side of the furnace. I.e. the inert or reducing gas is preferably supplied counter flow. The gas supplied may
5 include argon, N₂, H₂, CO, CO₂ or any mixture of them. For instance H₂/N₂ having relations such as 5:95, 20:80, 40:60, 80:20, and 95:5 by vol. . In one embodiment the atmosphere comprises 20-60 vol % of H₂ and balance N₂. Such atmosphere may reduce N₂ uptake, compared to e.g. H₂/N₂ (5:95), and it may increase the density of the reduced pellets. The atmosphere may also be supplied with CO, e.g. from burning natural gas.
10 Of course, other gas mixes being inert or reducing may be supplied to the furnace.

Preferably the method further includes the step:

c) cooling the reduced briquettes in a non-oxidising atmosphere (e.g. reducing
15 or inert) to a temperature below 200 °C , more preferably below 150 °C, preferably in an inert atmosphere.

The atmosphere during cooling may e.g. be argon, N₂, H₂, or any mixture of H₂/N₂ (e.g. 5:95 by vol.). Other atmospheres may also be employed. If it is desirable to have very
20 low levels of nitrogen in the briquettes, the briquettes may be cooled in a nitrogen free atmosphere such as for example an argon gas atmosphere.

In one embodiment briquetting is performed at a briquetting pressure in the range of 80-1000 kg/cm², preferably 100-500 kg/cm².

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In one embodiment briquetting is performed at a briquetting pressure in the range of 1000-10000 kg/cm², preferably 2000-5000 kg/cm².

Preferably the briquetting machine is a roller press. However, other kinds of briquetting
30 machines may be used.

Optionally the green briquettes are heat treated at a lower temperature before reduction. Preferably heat treating the green briquettes at a temperature in the range of 200-800 °C, more preferably 400-700 °C. Preferably, the optional heat treating at lower temperature is performed from 10 minutes to less than 2 hours, preferably less than 1 hour. By heat-
5 treating at lower temperatures the optional lubricant (if present) can be burned off in a controlled manner. In addition molybdenum trioxide (if present) may be reduced to molybdenum dioxide. This may be employed as a pre-reduction step prior to the reduction described in the previous paragraph or when producing partially reduced briquettes. The optional heat treating at 200-800 °C, can be performed in the same
10 furnace as the reduction. The optional heat treating and optional drying may also be combined.

Optionally, lubricants and/or binders and/or slag formers and/or desulfurizer can be added when mixing. The optional binders may be organic or inorganic binders. The binders may e.g. be a carbon containing binders partially replacing the carbonaceous
15 powder. Other binders may e.g. be bentonite and/or dextrin and/or sodium silicate and/or lime and/or gelatin. The optional slag former may be limestone, dolomite, and/or olivine. The total amount of lubricants and/or binders and/or slag formers and/or desulfurizers can be 0.1-10 % by weight of the dry matter content of the green briquette, more preferably less than 5 wt%. It may be in the range of 1-10 % by weight. The
20 binders are optional since the green briquettes by the water and iron addition becomes sufficiently strong to be reduced in the reduction furnace without severely cracking. If added the lubricant is preferably added in amounts of 0.1-2 % of the the dry matter content of the briquette, e.g. about 0.5-1 % by weight. The lubricant can e.g. be zinc stearate. However, other lubricants that are used in powder metallurgy may be added.

25 Depending on purities of the powders, the mixture the briquettes may contain further elements including oxides that are difficult to reduce. The amount of such elements are mainly determined by the purity of the tungsten containing powder and the optional molybdenum containing powder, but may also come from impurities in the iron powder,
30 the carbon powder, and from reactions with elements in the surrounding atmosphere during heating, reduction, or cooling.

The total process is endothermic and requires heat. To reduce the amount required external heat, oxygen gas or air can be provided in a pre-heating zone to react with the formed carbon monoxide to form carbon dioxide gas. If air is used the nitrogen uptake of the briquettes may increase. Using oxygen the nitrogen uptake during the heating and
 5 the reduction step can be minimised.

Instead of drying the green briquettes before entering the reduction furnace, the furnace may have a drying zone operating at a temperature in the range of 80-200 °C, preferably 100-150 °C.

10 The reduction furnace may also include a pre-reduction zone, downstream the drying zone if such is used, and operating in the range of 200-800 °C, preferably 400-700 °C.

The iron and tungsten containing green briquettes having a dry matter composition in weight-% of:

- 15 a) 90-100 of a mixture comprising in weight % of the mixture:
- | | |
|------------|--|
| 2-97 | tungsten containing powder containing at least one of tungsten oxides and tungsten carbides, |
| optionally | |
| 0.1-25 | carbon powder, |
| 2-90 | molybdenum containing powder, and |
| balance | |
| 1-40 | iron containing powder; |
- b) optionally
- | | |
|------|---|
| ≤ 10 | lubricant and/or binder and/or slag former and/or a |
| 25 | desulfurizer. |

Preferably the reduced iron and tungsten containing briquettes consisting of in weight %:

	W	3-97
	Mo+ W	50-97
5	O	≤ 10
	C	≤ 10
	Si	≤ 10
	Co	≤ 10
	Other elements	≤ 5
10	and balance Fe	2-40.

The briquettes can substitute for traditionally manufactured ferroalloys, when alloying with tungsten and optionally tungsten/molybdenum in melting practices. The briquettes can be produced at lower costs than standard grades of ferrotungsten. The briquettes dissolve quicker than standard grades of ferrotungsten. Depending on the reduction time, the relative amount of carbon in relation to the amount of reducible oxides, and the reduction temperature – the oxygen content in the briquettes can be partially or fully reduced. The briquettes can be easily transported on a conveying belt without the risk of rolling off.

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By briquetting before reduction it is possible to produce a briquette which has higher porosity than a briquette formed from reduced powders. Furthermore, it is possible to produce a briquette that is void of binders and lubricant.

25 Mixture

The mixture provided in step a) comprises (in weight-%):

	2-97	tungsten containing powder,
		optionally
	0.1-25	carbon powder,
30	2-90	molybdenum containing powder,
	Balance	
	1-40	iron containing powder.

Preferably the iron powder is 2-25 % by weight, more preferably 3-15 % by weight.
Preferably the tungsten containing powder is at least 20 % by weight.

5

Preferably, the tungsten containing powder + molybdenum containing powder is more than 50 % by weight of the mixture, more preferably more than 70 % by weight of the mixture.

10 In one embodiment the mixture consists of (in weight-%):

1-40, preferably 3-15 of a iron containing powder, and
75-99, preferably 85-97 of a tungsten containing powder.

Preferably, the tungsten containing powder includes tungsten oxides and tungsten carbides. Preferably, the reducible oxides in the tungsten containing powder and the
15 iron containing powder are stoichiometric matched with carbon of the tungsten carbides, so that after a reduction the carbon content is less than 10 % by weight preferably less than 5 % by weight, more preferably less than 1 % by weight, most preferably less than 0.5 % by weight, and oxygen is less than 10 % by weight, preferably less than 5 % by weight, most preferably less than 3 % by weight.

20

Thereby iron and tungsten containing briquettes can be produced that essentially consists of iron and tungsten and unavoidable impurities.

Iron and tungsten containing briquettes that consist of iron and tungsten and
25 unavoidable impurities can also be produced from a mixture where tungsten carbides is partially or fully replaced by a carbon powder, i.e. so that carbon of tungsten carbides and/or carbon powder stoichiometric matches the reducible oxides in tungsten containing powder and the iron powder.

30 Iron and tungsten containing briquettes that consists of iron, tungsten and molybdenum and unavoidable impurities can be produced from the mixture by adding the optional molybdenum containing powder. Here, carbon from the tungsten carbides and/or carbon

powder is stoichiometric matched with the reducible oxides in molybdenum containing powder, the tungsten containing powder and the iron powder. Here, the tungsten containing powder preferably is a tungsten carbide powder comprising at least 70 % by weight of WC, preferably at least 95 % by weight of WC, or a tungsten oxide powder comprising at least 70 % by weight of WO_3 , preferably at least 95 % by weight of WO_3 , or a mixture of these powders.

Preferably the carbon and oxygen is balanced so that after reduction, the carbon content is less than 10 % by weight preferably less than 5 % by weight, more preferably less than 1 % by weight, most preferably less than 0.5 % by weight, and oxygen is less than 10 % by weight, preferably less than 5 % by weight, most preferably less than 3 % by weight.

The relative amounts of molybdenum and tungsten can be varied by changing the relative amounts of the tungsten containing powder and molybdenum containing powder, while considering the carbon and oxygen balance.

In a preferred embodiment the weight ratio between tungsten carbide and tungsten oxide (WC/ WO_3) is within the range of 0.5-5, preferably 1-4, more preferably 1.5-3. An optimal balance is about 2. Thereby the tungsten carbide can match the tungsten oxide without the need of carbon powder addition.

In one embodiment the weight ratio between molybdenum and tungsten (Mo/W) are determined to be within the range 0.25 - 4, preferably 0.5 - 2, more preferably 0.8-1.25.

Tungsten containing powder

The tungsten containing powder is preferably one of:

- a tungsten carbide containing powder,
- a tungsten oxide containing powder,
- a mix of tungsten carbide containing powder and tungsten oxide containing powder.

Tungsten carbide containing powder

The tungsten carbide containing powder is a powder that comprises tungsten carbides contained in a metal matrix. Preferably the tungsten carbide containing powder is
5 obtained from tungsten cemented carbide scrap. The tungsten carbide containing powder preferably comprises 1-10 % by weight of carbon, balance tungsten and incidental impurities. The tungsten carbide containing powder may also include alloy elements which have formed a matrix (binding material) for the cemented tungsten carbide material. The proportion of carbide phase is generally between 70-97% of the
10 total weight of the composite. The carbon is present in the powder particles in the form of tungsten carbide grains, and typically the grain size averages between 0.10 μm and 15 μm . Any powder particle may include several tungsten carbide grains, in particular if the particle sizes are large. Further, the tungsten carbide containing powder may include powder particles that are void of any tungsten carbide grains; however most of the
15 powder particles will include one or more grains of tungsten carbide.

Some tungsten carbide powder can contain cobalt up to 15 % by weight; typically around 1-10 % by weight of Co. For instance, the tool material in circuit board drills typically comprises fine grained, cemented tungsten carbides existing in a cobalt matrix,
20 the amount of which represents 6 percent of the total weight of the tool material, while coarse grain tungsten carbide materials typically are used for the tool material of mine drills, where the cobalt content of the cemented carbide material is about 10 weight-%. These powders can be used if cobalt can be allowed or is desirable in the briquette to be produced. If not, these powders can be used after being leached from cobalt. For
25 instance a commercially available tungsten carbide containing powders from scrap that comprises 1-10 % by weight Co, usually in amounts of 3-8 % by weight Co, can be hydrometallurgical leached to reduce the cobalt content to be less than 1 % by weight Co, preferably less than 0.5 % by weight Co, more preferably less than 0.2 % by weight Co. The cobalt from the leaching process can be recycled and employed as a
30 commercial product per se.

Of course a tungsten carbide powder that already is low or void of cobalt can be used.

I.e. a powder that contains less than 1 % by weight Co, more preferably less than 0.5 % by weight Co, even more preferably less than 0.2 % by weight Co.

5 Preferably the tungsten carbide powder contains at least 90 % by weight of WC, more preferably at least 95 % by weight.

10 Preferably at least 90 % by weight, more preferably at least 99 % by weight, of the particles of the tungsten carbide containing powder pass through a test sieve in accordance to ISO 3310-1:2000 having nominal aperture sizes of 250 μm , more preferably 125 μm , most preferably 90 μm . Very fine powder where at least 99 % by weight, passes through a test sieve of 45 μm can suitably be used.

Tungsten oxide containing powder

15 The tungsten oxide containing powder may be an iron and tungsten oxide containing powder, more preferably iron tungstate in the form of the mineral Ferberite. Preferably a feberite that contains over 60 % of WO_3 , more preferably at least 70 % WO_3 . The ferberite is crushed and/or milled and/or ground to a powder so that at least 80 % by weight of the particles, preferably at least 90 %, passes through a test sieve in accordance to ISO 3310-1:2000 having nominal aperture sizes of 250 μm , more
20 preferably 125 μm .

The tungsten oxide containing powder may also be a pure tungsten oxide powder containing less than 5 % by weight of other elements besides W and O, preferably less than 1 % by weight of other elements. E.g. a powder that includes at least 95 % by
25 weight of WO_3 , preferably at least 99 % by weight.

30 Preferably at least 80 % by weight of the particles, more preferably at least 90 % by weight of the particles of the tungsten oxide powder pass through a test sieve in accordance to ISO 3310-1:2000 having nominal aperture sizes of 250 μm , more preferably 125 μm . most preferably 90 μm . Very fine powder where at least 99 % by weight, passes through a test sieve of 45 μm can suitably be used.

The tungsten oxide containing powder may also be a mix of iron tungstate and pure tungsten oxide powder.

Other available grades of tungsten oxide powders may also be used.

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Molybdenum containing powder

The molybdenum containing powder is preferably a molybdenum oxide powder. The powder preferably consists of molybdenum dioxide and/or molybdenum trioxide powder.

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The molybdenum oxide powder should contain 50-80 % by weight of Mo, the remaining elements being oxygen and impurities. Preferably the impurities are less than 10 % by weight, more preferably less than 5 % by weight, most preferably less than 1% by weight.

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Preferably at least 90 % by weight, more preferably at least 99 % by weight, of the particles of the molybdenum oxide powder pass through a test sieve in accordance to ISO 3310-1:2000 having nominal aperture sizes of 250 μm , more preferably 125 μm , most preferably 45 μm .

20 Iron containing powder

The iron containing powder is preferably an iron powder containing at least 80 wt% metallic iron, preferably at least 90 wt% metallic iron, more preferably at least 95 wt% metallic iron, most preferably at least 99 wt% metallic iron. The iron powder can be an iron sponge powder and/or a water atomised iron powder and/or a gas atomised iron powder and/or an iron filter dust and/or an iron sludge powder. For instance filter dust X-RFS40 from Höganäs AB, Sweden is a suitable powder.

25

The iron powder may partly or fully be replaced by an iron oxide powder, for instance but not limited to: powder consisting of one or more from the group of FeO , Fe_2O_3 ,

30 Fe_3O_4 , $\text{FeO}(\text{OH})$, $(\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O})$. The iron oxide powder may e.g. be mill scale.

Preferably, the iron containing powder contains at least 50 % by weight of metallic iron,

more preferably at least 80 wt% metallic Fe, most preferably at least 90 wt% metallic Fe.

The iron containing powder may also be a ferberite, FeWO_4 . It may also be a mix
5 between one or more powders of FeO , Fe_2O_3 , Fe_3O_4 , $\text{FeO}(\text{OH})$, $(\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O})$, FeWO_4 , and Fe.

Preferably at least 90 % by weight, more preferably at least 99 % by weight, of the
particles of the iron containing powder pass through a test sieve in accordance to ISO
10 3310-1:2000 having nominal aperture sizes of 125 μm , more preferably 90 μm . Very
fine powder where at least 99 % by weight, passes through a test sieve of 45 μm can
suitably be used.

Optional carbon powder

- 15 The green briquettes preferably includes a carbon source. In the preferred embodiment
the carbon source is a tungsten carbide containing powder, where the carbon content
stoichiometric matches the oxide contents in the green briquettes. However, a carbon
powder may also be used as the carbon source, either in combination with a tungsten
carbide containing powder or as the sole carbon source.
- 20 The carbon powder is preferably chosen from the group of: sub-bituminous coals,
bituminous coals, lignite, anthracite, graphite, coke, petroleum coke, and bio-carbons
such as charcoal, or carbon containing powders processed from these resources. The
carbon powder may e.g. be soot, carbon black, activated carbon. The carbon powder can
also be a mixture of different carbon powders.
- 25 Regarding the choice of carbon powder, the reactivity of the carbon is preferably taken
into consideration. Preferably carbon black is used. German brown coal (lignite),
charcoal, bituminous and sub-bituminous coals also have comparably high reactivity.
Graphite is also suitable.
- 30 Preferably at least 90 % by weight, more preferably at least 99 % by weight, of the
particles of the carbon powder pass through a test sieve in accordance to ISO 3310-

1:2000 having nominal aperture sizes of 125 μm , more preferably 45 μm , most preferably 20 μm .

The amount of the carbon source (i.e. WC-powder and/or carbon powder) is preferably determined by analysing the amount of reducible oxides in the tungsten containing powder, the iron powder, and the optional molybdenum containing powder. Preferably the amounts of the carbon source is chosen to stoichiometric match or slightly exceed the amount of reducible oxides in the tungsten containing powder, the iron powder, and the optional molybdenum containing powder. However, the amount of the carbon source may also be sub-stoichiometric.

10

The amount of the carbon source can be optimised by measuring the carbon levels and the oxygen levels in the reduced briquettes - increasing or decreasing the amount of carbon source to achieve desired levels of carbon and oxygen. Oxides which are difficult to reduce with carbon such as Si, Ca, Al, and Mg may be allowed up to certain levels depending on in which applications the briquettes are to be used in. For instance in many applications of steel metallurgy these oxides can be handled e.g. by removing them in the slag of steel melt. If lower amounts of these oxides and elements are desired, purer grades of the tungsten containing powder, the iron powder, and the optional molybdenum containing powder can be used, e.g. grades that contains less or no amounts of these oxides.

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Iron and tungsten containing green briquettes

The green briquettes comprises of the mixture provided in step a). When preparing the mixture the total amount of added water is around 1-10 % by weight of the mixture, more preferably 2-5 % by weight. The green briquettes may be dried to reduce the moisture content to less than 5 % by weight, or less than 3 % by weight.

25

The green briquettes may optionally comprise up to 10 % by weight of one or more organic or inorganic binders and/or slag formers and/or desulfurizers and/ or lubricants. In one embodiment the green briquettes are void of lubricants, binders, slag formers and desulfurizers.

30

The green briquettes are surprisingly strong and it may therefore be possible to use the dried green briquettes to directly alloy a steel melt with tungsten and optionally tungsten and molybdenum, i.e. without prior reduction of the green briquettes. The green
 5 briquettes can be cost efficient way of alloying with tungsten and optionally tungsten and molybdenum. The green briquettes may also be partially or fully reduced in by heating the green briquettes in subsequent steps.

Iron and tungsten containing briquettes

10 Iron and tungsten containing briquettes can be produced by the suggested process that consists of in weight %:

W	3-97, preferably 30-95,
Mo+ W	50-97, preferably 70-95,
O	≤ 10 , preferably ≤ 5 , more preferably ≤ 3 ,
15 C	≤ 10 , preferably ≤ 5 , more preferably ≤ 1 ,
Si	≤ 10 , preferably ≤ 5 , more preferably ≤ 1 ,
Co	≤ 10 , preferably ≤ 5 , more preferably ≤ 1 ,
Other elements	≤ 5 , preferably ≤ 1 ,

and balance Fe 2-40, preferably 3-25, more preferably 5-20, most preferably 5-15.

20

These briquettes have a geometric density in the range of 2-6 g/cm³, preferably 4-5.5 g/cm³.

O, C may be present from 0.05 % and higher. Si, Co may be present from traces up to
 25 the given amounts. They are preferably not deliberately added but may be present as impurities. Other elements apart from W, Mo, Fe, O, C, Si, Co may be present from traces up to the given amounts. They are preferably not deliberately added but may be present as impurities.

30

According to one example the iron and tungsten containing briquettes consists of in weight %:

- W 60-97, preferably 80-95,
 O ≤ 10 , preferably ≤ 5 , more preferably ≤ 3 ,
 5 C ≤ 10 , preferably ≤ 5 , more preferably ≤ 1 ,
 Si ≤ 10 , preferably ≤ 5 , more preferably ≤ 1 ,
 Co ≤ 10 , preferably ≤ 5 , more preferably ≤ 1 ,
 Other elements ≤ 5 , preferably ≤ 1 ,
 and balance Fe 2-40, preferably 3-25, more preferably 5-20, most preferably 5-15.

10

These briquettes have a geometric density in the range of 2-8 g/cm³, preferably 3-7 g/cm³, more preferably 4-6 g/cm³. The geometric density may be in the range of 4.5-5.5 g/cm³.

- 15 These briquettes may substitute traditionally manufactured ferrotungsten alloys, when alloying with tungsten in melting practices. The briquettes can be produced at lower costs than standard grades of ferrotungsten. Furthermore, due to their porous structures the briquettes dissolves quicker than standard grades of ferrotungsten.

- 20 According to another example the iron and tungsten containing briquettes consists of in weight %:

- W 20-80, preferably 30-65, more preferably 40-55,
 Mo 20-80, preferably 30-65, more preferably 40-55,
 Mo + W > 50 , preferably > 70 ,
 O ≤ 10 , preferably ≤ 5 , more preferably ≤ 3 ,
 25 C ≤ 10 , preferably ≤ 5 , more preferably ≤ 1 ,
 Si ≤ 10 , preferably ≤ 5 , more preferably ≤ 1 ,
 Co ≤ 10 , preferably ≤ 5 , more preferably ≤ 1 ,
 Other elements ≤ 5 , preferably ≤ 1 ,
 and balance Fe 2-40, preferably 3-25, more preferably 5-20, most preferably 5-15.

30

Preferably, the weight ratio of molybdenum and tungsten (Mo/W) are determined to be within the range 0.25 - 4, preferably 0.5 – 2, more preferably 0.8-1.25.

These briquettes have a geometric density in the range of 1-6 g/cm³, preferably 2-5 g/cm³.

- 5 These iron, tungsten and molybdenum containing briquettes are suitable for alloying with tungsten and molybdenum in melting practices. The iron, tungsten and molybdenum containing briquettes can be produced at comparably lower costs. Furthermore, due to their porous structures the briquettes dissolves quickly in a steel melt.
- 10 The amount of other elements is mainly controlled by the purity of the tungsten containing powder and the optional molybdenum containing powder. The purity of the iron containing powder and optional carbon powder may of course influence the amount of other elements.
- 15 The nitrogen content mainly depends on the nitrogen levels in the atmosphere during heating, reduction and cooling of the briquettes. By controlling the atmosphere in these steps the nitrogen content can be made lower than 0.5 wt%, preferably lower than 0.1 wt% and most preferably lower than 0.05 wt%.
- 20 **EXAMPLE**
- 1/3 by weight of WO₃ powder was mixed with 2/3 by weight of a WC powder. To the mixture 5 % by weight of Fe powder was added. The amounts, particle sizes and the purity of the powders are shown in Table 1. When mixing the powders, 5 % by weight of water was added

25 Table 1

Powder	Weight [g]	Particle size [μm]
WO ₃ (WO ₃ > 99.5%)	32	<45
WC (WC > 98%)	64	< 45
Fe (Fe > 99%)	10	<40

The mixture was thereafter fed to a briquetting press. The produced green briquettes where thereafter dried to a moisture content less than 3 % by weight.

- 5 The green pellets were reduced in a batch furnace at a temperature of 1200 °C for a time period of 2 hours, in a 95 vol-% N₂ and 5 vol-% H₂ atmosphere. The briquettes were thereafter allowed to cool to a temperature around 100 °C before evacuating the atmosphere and removal from the furnace. The average geometric density of the reduced briquettes was determined to be 5.9 g/cm³ as measured according to ASTM 962-08.

CLAIMS

1. A process for producing iron and tungsten containing briquettes the process including the steps of:
- 5 a) providing a mixture comprising (in weight-%):
- 2-97 tungsten containing powder containing at least one of tungsten oxides and tungsten carbides.
- optionally
- 0.1-25 carbon powder,
- 10 2-90 molybdenum containing powder,
- balance
- 1-40 iron containing powder.
- b) adding to the mixture:
- 15 a liquid, preferably water,
- optionally one or more of:
- lubricant,
- binder,
- slag former,
- 20 desulfurizer;
- c) briquetting to provide a plurality of green briquettes.
- 25
2. A process according to claim 1 wherein the mixture fulfilling the condition:
- > 50 molybdenum containing powder + tungsten containing powder.
- 30

3. A process according to claim 1 and 2 wherein the process further includes drying the green briquettes at a temperature less than 200 °C, preferably less than 150 °C, until the moisture content is less than 10 % by weight of the briquettes, preferably less than 5 % by weight.

5

4. A process according to any one of claims 1- 3 wherein the process further includes reducing the green briquettes at a temperature in the range of 800-1500 °C, preferably 1050-1400 °C, more preferably 1100-1300 °C, most preferably 1150-1250 °C.

10

5. A process according to claim 4, wherein the method includes one or more of the following steps:

- d) cooling the reduced briquettes in a non-oxidising atmosphere to a temperature below 200 °C , more preferably below 150 °C, preferably in an inert atmosphere;

15

6. Iron and tungsten containing green briquettes having a dry matter composition in weight-% of:

20

- a) 90-100 of a mixture comprising in weight % of the mixture:

2-97 tungsten containing powder containing at least one of tungsten oxides and tungsten carbides,

optionally

0.1-25 carbon powder,

2-90 molybdenum containing powder

25

balance

1-40 iron containing powder;

- b) optionally up to 10 of a binder and/or slag former and/or a desulfurizer.

30

7. Iron and tungsten containing briquettes consisting of in weight %:
- | | | |
|----|----------------|-----------|
| 5 | W | 3-97 |
| | Mo+ W | 50-97 |
| | O | ≤ 10 |
| | C | ≤ 10 |
| | Si | ≤ 10 |
| 10 | Co | ≤ 10 |
| | Other elements | ≤ 5 |
- and balance Fe 2-40.
8. Iron and tungsten briquettes according to claim 7 consisting of in weight %:
- | | | |
|----|----------------|--|
| 15 | W | 60-97, preferably 80-95, |
| | O | ≤ 10 , preferably ≤ 5 , more preferably ≤ 3 , |
| | C | ≤ 10 , preferably ≤ 5 , more preferably ≤ 1 , |
| | Si | ≤ 10 , preferably ≤ 5 , more preferably ≤ 1 , |
| | Co | ≤ 10 , preferably ≤ 5 , more preferably ≤ 1 , |
| 20 | Other elements | ≤ 5 , preferably ≤ 1 , |
- and balance Fe 2-40, preferably 3-25, more preferably 5-20, most preferably 5-15.
9. Iron and tungsten containing briquettes according to claim 7 consisting of in weight %:
- | | | |
|----|--------|--|
| 25 | W | 20-80, preferably 30-65, more preferably 40-55, |
| | Mo | 20-80, preferably 30-65, more preferably 40-55, |
| | Mo + W | > 50 , preferably > 70 , |
| | O | ≤ 10 , preferably ≤ 5 , more preferably ≤ 3 , |
| 30 | C | ≤ 10 , preferably ≤ 5 , more preferably ≤ 1 , |
| | Si | ≤ 10 , preferably ≤ 5 , more preferably ≤ 1 , |
| | Co | ≤ 10 , preferably ≤ 5 , more preferably ≤ 1 , |

Other elements ≤ 5 , preferably ≤ 1 ,
and balance Fe 2-40, preferably 3-25, more preferably 5-20, most preferably 5-15.

AMENDED CLAIMS**received by the International Bureau on 19 November 2014 (19.11.2014)**

1. A process for producing iron and tungsten containing briquettes the process including the steps of:
- 5 a) providing a mixture comprising (in weight-%):
- 2-97 tungsten containing powder containing at least one of tungsten oxides and tungsten carbides.
- optionally
- 0.1-25 carbon powder,
- 10 2-90 molybdenum containing powder,
- balance
- 1-40 iron containing powder.
- b) adding to the mixture:
- 15 water,
- optionally one or more of:
- slag former,
- desulfurizer;
- 20 c) briquetting to provide a plurality of green briquettes.
2. A process according to claim 1 wherein the mixture fulfilling the condition:
- > 50 molybdenum containing powder + tungsten containing powder.
- 25
3. A process according to claim 1 and 2 wherein the process further includes drying the green briquettes at a temperature less than 200 °C, preferably less than 150 °C, until the moisture content is less than 10 % by weight of the briquettes, preferably less than 5 % by weight.
- 30
4. A process according to any one of claims 1- 3 wherein the process further includes reducing the green briquettes at a temperature in the range of 800-1500 °C, preferably 1050-1400 °C, more preferably 1100-1300 °C, most preferably 1150-1250 °C.
- 35

5. A process according to claim 4, wherein the method includes one or more of the following steps:
- d) cooling the reduced briquettes in a non-oxidising atmosphere to a temperature below 200 °C , more preferably below 150 °C, preferably in an inert atmosphere;
6. Iron and tungsten containing green briquettes having a dry matter composition in weight-% of:
- a) 90-100 of a mixture comprising in weight % of the mixture:
- | | |
|------------|--|
| 2-97 | tungsten containing powder containing at least one of tungsten oxides and tungsten carbides, |
| optionally | |
| 0.1-25 | carbon powder, |
| 2-90 | molybdenum containing powder |
| balance | |
| 1-40 | iron containing powder; |
- b) optionally up to 10 of a slag former and/or a desulfurizer.
7. Iron and tungsten containing briquettes consisting of in weight %:
- | | |
|----------------|-------|
| W | 3-97 |
| Mo+ W | 50-97 |
| O | ≤ 10 |
| C | ≤ 10 |
| Si | ≤ 10 |
| Co | ≤ 10 |
| Other elements | ≤ 5 |
- and balance Fe 2-40.
8. Iron and tungsten briquettes according to claim 7 consisting of in weight %:
- | | |
|----------------|--|
| W | 60-97, preferably 80-95, |
| O | ≤ 10, preferably ≤ 5, more preferably ≤ 3, |
| C | ≤ 10, preferably ≤ 5, more preferably ≤ 1, |
| Si | ≤ 10, preferably ≤ 5, more preferably ≤ 1, |
| Co | ≤ 10, preferably ≤ 5, more preferably ≤ 1, |
| Other elements | ≤ 5, preferably ≤ 1, |

and balance Fe 2-40, preferably 3-25, more preferably 5-20, most preferably 5-15.

9. Iron and tungsten containing briquettes according to claim 7 consisting of in weight %:

5	W	20-80, preferably 30-65, more preferably 40-55,
	Mo	20-80, preferably 30-65, more preferably 40-55,
	Mo + W	> 50, preferably >70,
	O	≤ 10 , preferably ≤ 5 , more preferably ≤ 3 ,
10	C	≤ 10 , preferably ≤ 5 , more preferably ≤ 1 ,
	Si	≤ 10 , preferably ≤ 5 , more preferably ≤ 1 ,
	Co	≤ 10 , preferably ≤ 5 , more preferably ≤ 1 ,
	Other elements	≤ 5 , preferably ≤ 1 ,
15		and balance Fe 2-40, preferably 3-25, more preferably 5-20, most preferably 5-15.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/SE2014/050654

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, C22B, C22C

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)

EPO-Internal, PAJ, WPI data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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A	US 20030106395 A1 (LEITNER JURGEN), 12 June 2003 (2003-06-12); abstract --	1-9
A	WO 2011053231 A1 (MINPRO AKTIEBOLAG ET AL), 5 May 2011 (2011-05-05); abstract --	1-9



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

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“O” document referring to an oral disclosure, use, exhibition or other means

“P” document published prior to the international filing date but later than the priority date claimed

“T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

“X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

“Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

“&” document member of the same patent family

Date of the actual completion of the international search

12-09-2014

Date of mailing of the international search report

15-09-2014

Name and mailing address of the ISA/SE

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INTERNATIONAL SEARCH REPORTInternational application No.
PCT/SE2014/050654

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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Continuation of: second sheet

International Patent Classification (IPC)

B22F 3/00 (2006.01)

C22B 5/12 (2006.01)

C22B 34/36 (2006.01)

C22C 35/00 (2006.01)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

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