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(71) Applicant: HÖGANÄS AB (PUBL) [SE/SE]; Bruksgatan 35, 263 83 Höganäs (SE).

(72) Inventors: MAROLI, Barbara; Björkvägen 22, 263 32 Höganäs (SE). FRYKHOLM, Robert; Månskensgatan 32, 254 73 Ödåkra (SE). BENGTTSSON, Sven; Bergsgatan 22, 263 39 Höganäs (SE). FRISK, Karin; Movägen 21, 182 49 Enebyberg (SE).

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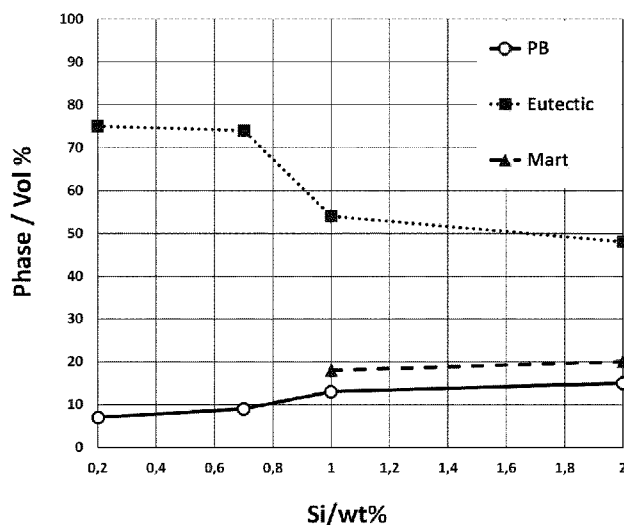


Fig. 4

(57) **Abstract:** The present invention relates in one aspect to an iron-based alloy composition comprising: boron (B): 1.6-2.4 wt.%; carbon (C): 1.7-3.0 wt.%; molybdenum (Mo): 16.0-19.5 wt.%; nickel (Ni): 3.5-6.5 wt.%; manganese (Mn): below 0.8 wt.%; silicon (Si): 0.2-3.0 wt.%; vanadium (V): 10.8-13.2 wt.%; and balanced with iron (Fe). In a further aspect the invention relates to an item comprising a substrate portion and a hardfacing coating bonded to the substrate portion, wherein the hardfacing coating is made by an overlay welding process using the iron-based alloy composition.

Wear-resistant iron-based alloy compositions comprising Nickel

The present invention relates in one aspect to an iron-based alloy composition for hardfacing applications. In a further aspect the invention relates to a hardfacing coating made from an iron-based alloy composition. In a yet further aspect the invention relates to a method of hardfacing an item using an iron-based alloy composition as a coating material. Furthermore, in one aspect, the invention relates to hardfacing by overlay welding using an iron-based alloy composition as a coating material. In a particular aspect, the invention relates to hardfacing by laser cladding using an iron-based alloy composition as a coating material. In another particular aspect, the invention relates to hardfacing by plasma arc transfer (PTA) welding using an iron-based alloy composition as a coating material.

BACKGROUND OF THE INVENTION

Hardfacing is a metallurgical technique to extend the lifetime of tools and other parts intended for use in very harsh operational conditions by providing the most exposed portions of such items with a wear resistant coating layer. For example, the coating may be applied to selected surface regions as a protective layer in the production of new parts, or may be applied to restore worn surfaces in a repair process. Typically, a hardfacing coating is applied as an overlay welded layer metallurgically bonded to a substrate portion of an item.

Hardfacing materials are complex alloys that are usually designed for particular applications in order to provide protection against deterioration mechanisms, such as abrasive wear, impact wear, and erosion. Typical applications may include, but are not limited to oil and gas drilling, mining, cement production, agricultural and earth-moving machinery, moulding tools, and turbine components for e.g. aerospace and power generation. However, many of the best performing known hardfacing materials have several drawbacks including high cost, environmental impact, and very limited resistance when it comes to combined wear scenarios, where different types of wear mechanism contribute in combination to the deterioration of the item under realistic operational conditions.

Different techniques for applying a hardfacing coating to a substrate exist. One of the challenges in this context is that each technique has process type specific characteristics influencing the properties of the obtained coating, and thus the actually achieved wear resistance. For example, laser cladding processes have the advantage of fast application with a relatively small heat affected zone and a low degree of substrate dilution as compared to other types of overlay welding techniques. However, these characteristics are linked to a relatively fast cooling rate of the welding melt pool and entail an increased tendency to the formation of cracks and/or porosity to occur in the coating. An increased tendency to crack formation and porosity may lead to excessive wear as compared to e.g. process using the slower plasma transferred arc (PTA) welding technique. The PTA-technique, on the other hand, may lead to a larger heat affected zone, increased dilution from the substrate and risk for distortion of the part to be coated. Therefore, there is a need for alloy compositions that can easily be adapted to or even optimized for a particular hardfacing technique in order to achieve coatings with a significantly reduced tendency to pore and crack formation, and most preferably resulting in pore and crack free coatings with combined resistance to abrasive and impact wear.

Some of the issues mentioned above have been addressed in previous studies published by the inventors, see e.g.: Maroli et al. on "Effect of Type and Amount of Tungsten Carbides on the Abrasive Wear of Laser Cladded Nickel Based Coatings", Int. Thermal Spray Conf. - ITSC 2015, Long Beach, CA, USA; Bengtsson et al. on "New Hardfacing Material with High Impact Wear Resistance", Int. Thermal Spray Conf. - ITSC 2016, Shanghai; Maroli et al. on "Iron Based Hardfacing Alloys for Abrasive and Impact Wear", Int. Thermal Spray Conf. – ITSC 2017, Düsseldorf, Germany; and Maroli et al. on "Cost Effective Iron Based Alloys for Abrasive Wear" Int. Thermal Spray Conf. – ITSC 2018, Orlando, USA. These studies present amongst others measurements quantifying the properties of certain iron-based alloys and their usefulness in cost effective hardfacing applications. Other studies have focussed on completely avoiding chromium as a component in hardfacing alloys; see e.g. Eibl, WO 2017/040775, relating to "Chromium Free and Low-Chromium Wear Resistant Alloys". However, even these improved alloy compositions may still face some of the above-mentioned limitations. In some applications, as for example coating of some

types of shear bars, steel rollers and forming dies cracks and porosity are not acceptable. Therefore, there is a continued need for finding alternatives, and preferably improved alloys for hardfacing, overcoming or improving on at least some of the above-mentioned issues.

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Furthermore, it has been found that the best performing ones amongst the known hardfacing alloys can be rather sensitive to the choice of welding technique and to the process parameters used for applying the hardfacing alloy as a coating to a substrate portion. At the same time, the available equipment for hardfacing may determine the processing type, and processing parameters may be subject to external constraints dictated by the complexity of a specific hardfacing task. A lack of tolerance with respect to changing processing parameters may pose yet another challenge for designing a hardfacing process to the desired outcome in terms of quality and wear resistance of the coating. It is therefore also desirable to provide a hardfacing alloy and method that is susceptible of coping with such factors, yet providing high wear resistance, in particular in a combined wear type scenario.

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SUMMARY OF THE INVENTION

A first aspect of the invention relates to an iron-based alloy composition comprising: boron (B): 1.6-2.4 wt.%; carbon (C): 1.7-3.0 wt.%; molybdenum (Mo): 16.0-19.5 wt.%; nickel (Ni): 3.5-6.5 wt.%; manganese (Mn): below 0.8 wt%; silicon (Si): 0.2-3.0 wt.%; vanadium (V): 10.8-13.2 wt.%; and balanced with iron (Fe).

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The iron-based alloy composition is for hardfacing a substrate by means of known hardfacing techniques, such as overlay-welding using e.g. plasma transfer arc (PTA) welding or laser cladding techniques. The alloy may be provided in any form suitable for being fed to and processed by the employed hardfacing apparatus into a hardfacing coating. Typical substrates are low-alloyed steel materials, such as those commonly used for tooling in any of the above-mentioned fields of application.

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The iron-based alloy composition is designed (a) to be easy to weld with few to no cracks and without detrimental porosity, (b) to provide high hardness, such as above 60HRC, high abrasive wear resistance, such as below 15 mm³, in ASTM G65 procedure A and good impact resistance, as well as (c) for stable microstructure control.

With Ni additions in the range as specified herein, the alloy becomes easier to apply in a cladding operation. At too low levels of Ni the material is prone to cracking, and at too high level the hardness drops. Within the suggested window a good combination of hardness and resistance to cracking is obtained. Si is optimized for balance between hard phases and eutectic structure. In fact, a particular merit of the present invention resides in the insight that Si can be used in a surprisingly efficient and reliable manner to control the formation of borides. The upper limit is set to ensure sufficient formation of the eutectic structure, which is necessary for sufficient hardness and wear resistance.

The advantages of adding Nickel and Silicon in combination, with the particular ranges selected for the Nickel and Silicon content include an improved versatility of the coating system as compared to known hardfacing alloys, due to a surprisingly effective combined wear resistance where different types of wear mechanisms as well as coating quality come into play, as seen e.g. in analyses of the hardness, abrasive wear resistance, impact wear resistance, pore formation, cracking tendency, and the like for hardfacing coating samples produced using the iron-based alloy composition according to embodiments of the invention. Apparently, the Si addition synergistically enhances the effect of Ni addition, and provides amongst others an enhanced tunability of wear related coating properties as compared to known compositions. A surprisingly simple tuning mechanism is observed within the ranges of Ni and Si content according to embodiments of the invention as disclosed herein, thereby providing a surprisingly effective control of coating properties. For example, this tuning mechanism allows for a well-controlled adaptation of the coating alloy system to specific requirements of a particular coating process to be used in a given application, without compromising the overall wear resistance performance of such a coating in a combined wear mechanism scenario. This allows a skilled person using the disclosed coating alloy system to design a coating alloy composition according to a desired wear resistance, e.g. by setting a desired Ni-content within the given range, and merely varying the Si content for a given Ni content in order to optimize the Si-content for the combined wear scenario of a given application. For example, the coating may be optimized for maximum hardness and abrasive wear resistance at lower Si-contents.

Alternatively, the skilled person designing a coating for a specific application may increase the Si-content in order to significantly reduce the tendency to crack formation in certain coating processes with high cooling rates of the melt pool during processing, such as cooling rates comparable to those encountered in typical laser cladding processes. A significant reduction in the tendency to pore and crack formation when preparing a hardfacing coating by laser cladding as compared to known compositions is indeed a striking effect of the combined addition of Ni and Si. This is achieved within carefully selected combinations of subranges for the Nickel content and for the Silicon content as further detailed below.

Further according to some embodiments of the iron-based alloy composition, the amount of silicon is 0.3-2.0 wt.%. This range of Si-content supports a good combined wear resistance with the possibility of tuning the wear resistance and coating quality properties of a hardfacing coating produced from the iron-based alloy composition over a broad range.

A minimum Si content of about 0.2 wt.%, or at least 0.3 wt.%, or at least 0.4wt% or at least 0.5wt% is beneficial for an improved behaviour of the alloy material in powder production, in particular when using atomization techniques, such as gas atomization or water atomization and during overlay welding.

Advantageously according to some embodiments of the iron-based alloy composition, the amount of silicon is 1.8 wt.% or below, preferably 1.5 wt.% or below, or 1 wt.% or below. Thereby, an enhanced tuning response to varying the Si content is achieved, which allows for a good control of a trade-off between, on the one hand, an extreme hardness/abrasive wear performance and, on the other hand, crack formation tendency with good hardness/abrasive wear performance. For example, the hardness and/or abrasive wear performance may be increased by reducing the Si-content towards the lower end of the range at the expense of an increased tendency to crack formation in certain processes. This may be useful if an extreme hardness and abrasive wear performance is desired, but where crack formation tendency is not so much an issue, e.g. in hardfacing processes like PTA welding, which traditionally have a larger processing spot than e.g. typical laser cladding processes, and a generally

lower associated cooling rate for the solidification of the molten coating material upon its application on the substrate.

5 As discussed in more detail below, an important insight underlying the present invention relies on an analysis of the microstructure of the processed alloys. The microstructure analysis reveals that the skilled person may use the present invention to design an alloy composition optimized for a particular application by setting the Nickel content of the iron-based alloy composition, and further adding Silicon within carefully selected ranges allowing for tuning the distribution of different phases in the micro-
10 structure of the processed material, in order to achieve desired properties of combined wear resistance including combinations of hardness, abrasive wear, impact wear, and/or coating quality (e.g. crack free / low porosity). Notably, Silicon was found to affect the amount of primary hard phase particles formed in the iron-based alloys with Ni additions, more particularly the amount of primary boride particles. A particularly
15 advantageous range for the Silicon content for tuning the alloy properties was found to occur below 1.5 wt.%, or below 1.4 wt.%, or below 1.3 wt.%, or below 1.2 wt.%, or below 1.1 wt.%, or below 1 wt.%, and above 0.2 wt.%, or above 0.3 wt.%, or above 0.4 wt.%, or above 0.5 wt.%, or above 0.6 wt.%.

20 Advantageously according to some embodiments of the iron-based alloy composition, the amount of silicon is at least 0.7 wt.%, preferably at least 1 wt.%, or at least 1.2 wt.%, or at least 1.5 wt.% or at least 1.8 wt.%. A higher Si content has the advantage that it synergistically with the addition of Ni reduces crack and pore formation tendency in a coating produced from the iron-based alloy composition, but still yields
25 satisfactory values for wear resistance for most hardfacing applications, including abrasive wear, impact wear and/or hardness. This is particularly useful for fast overlay welding processes with a high cooling rate of the melt pool in the processing spot, such as traditionally encountered in laser cladding applications, in particular in combination with a fast scan rate.

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Further according to some embodiments of the iron-based alloy composition, the amount of boron is 1.8-2.3 wt.%. Advantageously according to some embodiments the amount of boron is 1.8-2.2 wt.%.

Further according to some embodiments of the iron-based alloy composition, the amount of nickel is 4.2-6.1 wt.%. Advantageously according to some embodiments of the iron-based alloy composition, the amount of nickel is at least 4 wt.%, at least 4.5 wt.%, or at least 5 wt.%. Further according to some embodiments of the iron-based alloy composition, the amount of nickel is up to 5.5 wt.%, up to 6 wt.%, or up to 6.5 wt.%. Furthermore, according to some embodiments, the amount of Nickel is within any combination of a minimum amount of Nickel and a maximum amount of Nickel, wherein the minimum amount of Nickel is one of 4 wt.%, 4.5 wt.%, and 5 wt.%, and wherein the maximum amount of Nickel is one of 5.5 wt.%, 6 wt.%, and 6.5 wt.%.

Thereby the tendency to pore formation and/or cracking in a hardfacing coating produced from the iron-based alloy composition is significantly reduced without compromising too much on other wear resistance performance parameters, thus making the alloy versatile for use in numerous hardfacing applications and for use in a larger number of different hardfacing processes as compared to known hardfacing alloy compositions. This allows for reliable hardfacing processes with a stable processing result that is also more robust to intentional or un-intentional variations in processing parameters. A synergistic improvement in all these respects is achieved for the selected ranges of Ni content in combination with the addition of Si in agreement with the above-mentioned advantageous amounts, such as of at least 0.7 wt.%, preferably at least 1 wt.%, at least 1.3 wt.%, or at least 1.5 wt.%.

Advantageously according to some embodiments of the iron-based alloy composition, the amount of carbon is 1.8-2.4 wt.%. Reducing the amount of Carbon to the selected range reduces the risk of stabilizing an excessive amount of retained austenite in the matrix of the processed alloy at room temperature while ensuring a sufficient minimum amount of Carbon for adequate formation of primary carbides. Thereby, a desired hardness and/or combined wear resistance is more reliably achieved.

Further according to some embodiments, the iron-based alloy composition comprises impurities, wherein a total amount of the impurities in the iron-based alloy composition is below 1 wt.%. When producing an alloy in large batches on an industrial scale, remainders of impurities are typically unavoidable, but a total amount of the impurities in the iron-based alloy composition can typically be kept below 1 wt.%, or even below

0.5 wt.%. Generally, impurities are further components other than those specified as alloying elements making up the alloy composition. In the present case, any element other than the alloying elements B, C, Mo, Ni, Mn, Si, V, and Fe are considered as impurities in the iron-based alloy composition. Typical impurities include one or more of N, O, S, Cu, Co. Another example of an impurity is Cr, which in the iron-based alloy compositions as disclosed herein may be present in the alloy composition at an amount of up to 0.3 wt.%. Impurities may be unavoidable or intentionally added further components. The total amount of impurities will typically not exceed the above-mentioned ranges.

Further according to some embodiments of the iron-based alloy composition the alloy composition is a powder composition. Thereby, the iron-based alloy composition is suitable for use in powder-based hardfacing coating techniques. This includes e.g. compatibility with apparatus used for applying a hardfacing coating to a substrate, such as apparatus for powder-based PTA overlay-welding or for powder based laser cladding. The powder may, for example be prepared by any suitable known technique, such as by gas atomization. Specified particle size cuts may be prepared using standard techniques known in the art, such as using any known suitable sieving technique, according to predefined specifications for the particle size compatible with the powder feeding system of the hardfacing equipment.

Further according to some embodiments of the iron-based alloy composition, at least 95 wt.% of the powder composition has a particle size of up to 300 μ m, or up to 250 μ m, or up to 200 μ m, or up to 150 μ m, and/or wherein at least 95 wt.% of the powder composition has a particle size of at least 5 μ m, or at least 10 μ m, or at least 20 μ m, or at least 30 μ m, or at least 40 μ m, or at least 50 μ m, i.e.: according to some embodiments, at least 95 wt.% of the powder composition has a particle size of up to 300 μ m, or up to 250 μ m, or up to 200 μ m, or up to 150 μ m; furthermore, according to some embodiments, at least 95 wt.% of the powder composition has a particle size of at least 5 μ m, or at least 10 μ m, or at least 20 μ m, or at least 30 μ m, or at least 40 μ m, or at least 50 μ m; furthermore, according to some embodiments, at least 95 wt.% of the powder composition has a particle size within any combination of a specified minimum particle size and a specified maximum particle size, wherein the minimum particle size is one of 5 μ m, 10 μ m, 20 μ m, 30 μ m, 40 μ m, and 50 μ m, and wherein the maximum particle

size is one of 150µm, 200µm, 250µm, and 300µm. All particle sizes as specified herein are determined by dry sieving according to European Standard EN 24 497:1993 as approved by the European Committee for Standardization (CEN) on April 2, 1993, wherein EN 24 497:1993 endorses ISO 4497:1983.

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As mentioned above, a particle size cut is advantageously adapted according to specifications for compatibility with powder feeding devices of the coating apparatus to be used for applying the hardfacing coating.

10 The suitability for a powder-based hardfacing apparatus may further imply an overall maximum particle size not to be exceeded, which may lie above the upper limit for the specified particle size range, but where otherwise at least 95 wt.% fall within the specified range of particle sizes. Advantageously according to some embodiments of the iron-based alloy composition, at least 97 wt.%, or at least 98 wt.%, or at least 99 wt.%,
15 or at least 99.9 wt.% of all particles fall within the specified range of particle sizes. The overall maximum particle size not to be exceeded will depend on the actual specification of the powder-feed apparatus/mechanism to be used, and may for example be up to 350µm, up to 300µm, up to 250µm, or up to about 200µm. The particle size cut may be prepared by any suitable method known in the art of powder preparation, such
20 as sieving by using sieve cloths with different mesh sizes. As already mentioned above, all particle sizes as specified in this application are determined by dry sieving according to European Standard EN 24 497:1993 as approved by the European Committee for Standardization (CEN) on April 2, 1993, wherein EN 24 497:1993 endorses ISO 4497:1983.

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A further aspect of the invention relates to a coating produced by a hardfacing technique, such as overlay welding, using any of the alloy compositions disclosed herein. A further aspect of the invention relates to a coated item, the item comprising a coating bonded to a substrate portion thereof, wherein the coating is produced by a hardfacing
30 technique, such as overlay welding, using any of the alloy compositions disclosed herein.

According to some embodiments an item comprises a substrate portion and a coating bonded to the substrate portion, wherein the coating is made using an iron-based

alloy composition according to any one of the embodiments disclosed herein. The coating is for hardfacing of the substrate portion. Preferably, the coating is made by an overlay welding process.

- 5 Further according to some embodiments of the coated item, the coating is applied by an overlay welding process, such as a plasma transfer arc (PTA) welding process or a laser cladding process. As mentioned above, different hardfacing techniques may have process type specific characteristics influencing the wear resistance properties of the obtained coating. A particular advantage of the iron-based alloy compositions
- 10 according to embodiments of the invention arises when adapted to or even optimized for a particular hardfacing technique. Both PTA welding and laser cladding techniques have been proven to work particularly well for forming hardfacing coatings using embodiments of the iron-based alloy composition of the invention, wherein particularly advantageous respective ranges for use in combination with PTA welding or alternatively
- 15 in combination with laser cladding have been discussed above.

- Furthermore, the above-mentioned simple tuning mechanism may be used effectively for a well-controlled adaptation of the coating alloy system to specific requirements of the particular coating process to be used, without having to embark on a large investigation of the influence of the numerous further components contained in the alloy.
- 20 For example, the coating may be optimized for maximum hardness and abrasive wear resistance at lower Si contents, but may have a tendency to form pores or cracks at high cooling rates. Such a composition would be most useful in combination with PTA welding, wherein the relevant advantageous ranges for the Ni-content and for the Si-content are discussed above. In another example also discussed above, the skilled
- 25 person designing a coating for a specific application may increase the Si content in combination with the Ni-content in order to significantly reduce the tendency to pore and crack formation in certain coating processes involving high cooling rates, such as cooling rates comparable to those encountered in typical laser cladding processes.
- 30 Such a composition would be most useful for processes where laser cladding is preferred, wherein relevant advantageous ranges for the Ni-content and for the Si content are also discussed above.

Further according to some embodiments of the coated item, the dilution from the substrate material is below 20%, or below 15%, below 10%, or below 5%, or below 1%.

Further according to some embodiments of the coated item, the coating has a Rockwell hardness HRC of at least 60, at least 63, or at least 65.

Further according to some embodiments of the coated item, the coating has an abrasive wear resistance as determined according to ASTM G65, procedure A, of, below 15mm³, below 12mm³, or below 10mm³.

Further according to some embodiments of the coated item, the coating has an impact wear as determined according to the ball impact wear testing method of more than one strike for an impact energy per strike of 25J, more than 5 strikes for an impact energy per strike of 20J, more than 15 strikes for an impact energy per strike of 10J.

Further according to some embodiments of the coated item, the coating has a microstructure comprising primary boride and eutectic matrix material, wherein a ratio of an amount of primary boride by volume to an amount of eutectic matrix material by volume is below 0.3, or below 0.25. Further according to some embodiments of the coated item, the coating has a microstructure comprising primary boride and eutectic matrix material, wherein a ratio of an amount of primary boride by volume to an amount of eutectic matrix material by volume is at least 0.01, or at least 0.03.

As mentioned above, the hardfacing material is typically applied as a coating to a substrate portion of an item. Typical substrates are steel materials, such as used for tooling in any of the applications mentioned above, for example low alloy steel. Iron-based hardfacing materials are composite materials with a microstructure made up of so-called hard-phase particles that are embedded in a matrix of another hardphase. The hardfacing material is formed in a process of first melting an iron-based alloy composition, such as an iron-based alloy composition according to embodiments of the present invention, which is then allowed to cool down to solidify into the desired form, e.g. as a hardfacing coating. During cool-down, the hard-phase particles are formed prior to the matrix material, i.e. the hard-phase particles are formed by solidi-

fication at higher temperatures than the matrix . The hard-phase particles are therefore also referred to as “primary” hard-phases. When analysing the relative amounts of the different hard phases and matrix materials, the amounts are determined in percent by volume using standard metallurgical techniques based on image analysis.

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In hardfacing materials formed using the iron-based alloy composition according to embodiments of the invention, the hard-phase particles are primary carbides and primary borides, wherein elemental mapping as performed by the inventors points to a predominant formation of Vanadium rich carbide particles on the one hand and Molybdenum rich boride particles on the other hand. The elemental mapping performed by the inventors further indicates that the subsequently formed matrix material solidifies as a eutectic structure of Molybdenum rich boride intercalated with Martensite. However, metallurgical image analysis of micrographs held together with elemental mapping data also reveals that the matrix material further tends to comprise Molybdenum depleted islands, which coincide with regions of Boron depletion. These islands may thus be distinguished from regions of eutectic structure by an elemental mapping analysis of the coating material by energy dispersive spectroscopy (EDS). Island regions will appear as regions with a very low signal for Molybdenum and Boron. The EDS analysis is typically performed in a region that is representative of the coating, such as typically within a bulk region of the coating, using standard metallurgical image analysis techniques.

Without being bound by theory, these islands may be attributed to the formation of martensite, possibly with small amounts of retained austenite, which appear to occur as a consequence of Molybdenum and Boron being consumed by the formation of the primary boride particles, prior to the solidification of the matrix material. Moreover, the insight provided by the inventors suggests that the addition of Silicon directly affects the amount of primary borides formed in the hardfacing materials from processing the iron-based alloy composition according to embodiments of the invention, and thus that controlling the Si content is critical in determining the final microstructure of a hardfacing material. As a consequence, controlling the Si content is critical in determining the final properties of a coating. An important insight underlying the present invention is therefore that varying the Silicon content within carefully selected ranges directly affects the amount of primary borides formed at the expense of the

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amount of eutectic matrix material, which provides a direct handle for adapting the properties of a coating formed from the alloy composition according to embodiments of the invention, e.g. with respect to abrasive wear. For example, providing a first coating having a first ratio of the amount of borides over the amount of eutectic structure, and a second coating having a second ratio of the amount of borides over the amount of eutectic structure that is different as compared to the first ratio, will have different abrasive wear properties. According to embodiments of the present invention, the ratio of the amount of borides to the amount of eutectic structure, and thus the coating properties, may thus be controlled by varying the Silicon content, wherein increasing (lowering) the Silicon content lowers (increases) the resistance to abrasive wear slightly, yet reproducibly. If, e.g., the first ratio is larger than the second ratio, the abrasive wear resistance of the first coating will be lower (higher abrasive wear value when measured using the ASTM G65 procedure A test) as compared to the second coating, and vice versa.

A further aspect of the invention relates to a method of hardfacing a substrate, the method comprising the steps of: providing a substrate; and applying a coating to the substrate using an iron-based alloy composition according to any one of the embodiments disclosed herein as a coating material. Advantageously, the coating is applied by an overlay welding process. Thereby, the same advantages are achieved in an analogous manner, as discussed herein with respect to the iron-based alloy composition, and with respect to hardfacing coatings and coated items produced using the iron-based alloy composition according to any of the embodiments disclosed herein. Typical substrates are steel materials, such as used for tooling in any of the applications mentioned above, for example low alloy steel.

Further according to some embodiments of the method, the overlay welding process is a plasma transfer arc (PTA) welding process or a laser cladding process. Thereby, the same advantages are achieved in an analogous manner, as discussed above, with particular advantages arising from the combination of carefully selected ranges for the Ni-content and Si-content adapted for the specific use with PTA welding and laser cladding, respectively, as already discussed above.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention will be described in more detail in the following by referring to examples and the appended drawings, wherein the drawings show in

- 5 Fig. 1 an overview over die penetration test results for different alloy compositions applied as a hardfacing coating to a substrate by laser cladding;
- Fig. 2 die penetration test results for the alloy composition "Alloy 6" applied as a hardfacing coating to a substrate by laser cladding at higher speed;
- 10 Fig. 3a-d SEM micrographs showing the microstructure of four different alloys processed into ingot samples;
- Fig. 4 a graph showing the influence of the addition of Si on the microstructure of processed alloys;
- 15 Fig. 5 energy dispersive SEM micrographs showing elemental mapping of B, C, Si, V, Mn, Fe, Ni and Mo for one example of an alloy;
- 20 Fig. 6a-c cross-sectional SEM micrographs of overlay welds produced by laser cladding using three different alloys;
- Fig. 7 schematically, an arrangement for testing impact wear resistance according to the ball drop method; and in
- 25 Fig. 8 a graph plotting impact energy as a function of number of strikes to achieve the first crack, for alloy compositions Alloy 3, Alloy 6, and the reference alloy REF.

30 DETAILED DESCRIPTION

As mentioned above, one drawback of laser clad coatings made using known iron-based alloy compositions is the presence of large pores and cracks in the coating. Pores and cracks are detrimental for the coating properties. This is, for example, an issue of concern for applications requiring abrasive wear resistance, but also in many

other scenarios of resistance to a combination of different wear mechanisms. By optimizing the amount of Silicon in iron-based alloy compositions containing selected amounts of Nickel, issues of pore and crack formation in hardfacing coatings can be suppressed or at least mitigated.

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In the following, the invention is described by reference to exemplifying alloy compositions with systematically varied nickel (Ni) and silicon (Si) contents. Details of the alloy compositions are given in the MATERIAL section. Details of overlay welding procedures by plasma transfer arc (PTA) welding and laser cladding are given in the

10 PROCESS section. Analysis techniques for characterizing the properties of the processed alloys are described in the EVALUATION section. Analysis results are presented in the RESULTS section, including a discussion of the influence of adding Ni and Si to the iron-based alloy compositions according to embodiments of the present invention.

15

EXAMPLES

MATERIAL

Alloy powders, REF, 1-8, M9 and M10 with the chemical composition reported in Table 1 were investigated. The alloys were gas atomized and sieved between 53-

20

150 μ m for compatibility with powder feeding devices of the overlay welding equipment.

Alloy		C	B	Mo	V	Mn	Ni	Si	Fe
		wt.%	wt.%	wt.%	wt.%	wt.%	wt.%	wt.%	wt.%
REF	< 2%Ni	2.6	2.0	17.5	12.0	0.5	1.5	0.7	Bal
1	3%Ni	2.4	2.0	17.5	11.8	0.6	3.0	0.2	Bal
2	4%Ni	2.4	2.0	17.5	11.9	0.5	4.3	0.2	Bal
3		2.4	2.0	17.8	11.9	0.7	4.3	0.7	Bal
4		2.5	2.0	17.8	11.9	0.6	3.9	1.0	Bal
5		2.6	2.0	17.5	12.0	0.5	4.0	1.5	Bal
6	5%Ni	2.0	2.1	18.3	12.6	0.6	5.0	1.6	Bal
7	6%Ni	2.5	1.9	18.2	11.9	0.8	6.1	1.5	Bal
8	5%Ni	2.8	2.0	16.5	11.2	0.6	4.8	0.6	Bal
M9	5%Ni	2.4	2.0	17.9	11.9	0.7	5.2	0.9	Bal
M10	4%Ni	2.3	2.0	17.9	12.3	0.5	4.2	1.4	Bal
16	Ingot	2.4	1.8	16.9	12.2	0.43	3.8	0.2	Bal
17		2.6	1.9	18.5	11.8	0.40	4.2	0.8	Bal
18		2.5	1.9	18.1	12.6	0.43	4.0	1.1	Bal
19		2.3	2.0	17.2	12.5	0.48	4.1	2.1	Bal

Table 1: Chemical composition of investigated alloys

PROCESS

a) PTA welding

- 5 Alloy 1-8, M9, and M10 in Table 1 were deposited on EN S235JR mild structural steel plates using a commercial PTA unit (Commersald 300I). One layer, single track clads were deposited on a substrate with size 125x40x20 [mm] using the welding parameters in Table 2. A mix of Argon and 5%H₂ with flow rate of 16.5 l/min was used as shield gas to protect the melt pool from oxidation. Argon with flow of 2.0 l/min was used to transport the powder from the hopper to the melt pool. Pilot gas was 2.0 l/min.
- 10 The samples coated with the parameters in Table 2 were used for measurements of coating hardness, dilution and microstructure.

Substrate T(°C)	Feed rate g/min	Speed cm/min	Power A	Oscillation (mm/min)	Cooling
RT	25	8	125	10	Air

Table 2: PTA welding parameters for coating of 125x40x20 mm substrates, one layer, single track

Clads consisting of two overlapping tracks were deposited on a substrate with size 220x60x30 [mm]. Overlap between the two adjacent clads was 3 mm and oscillation of the PTA torch 10 mm. The clads were deposited using the welding parameters in

Table 3 on room temperature substrates. The coated samples were cooled in vermiculate. A mix of Argon and 5% H_2 with flow rate of 16.5 l/min was used as shield. Argon, flow 2.0 l/min was used as transport gas. Pilot gas was 2.0 l/min. Blanks with size requested by ASTM G65 were cut out from these samples, plane grinded and tested for resistance to abrasive wear.

Alloy	Substrate T(°C)	Feed rate g/min	Speed cm/min	Power A	Cooling
3, 5, 6	RT	25	8	120	Air

Table 3: PTA welding parameters for coating of 220x60x30mm substrates, one layer, two overlapping tracks

b) Laser cladding

Laser cladding was performed using an IPG 6 kW fibre coupled diode laser with a Coax 8 powder feed nozzle and a 5 mm round spot. The process window was typically determined using two laser travel speeds, 16 and 8 mm/s. Powder feed rate was designed to give approximately 1 mm thick coatings. The laser power was varied between 1000 to 2500W. Argon, 15 l/min, was used as shielding gas. Argon, 6 l/min, was used as transport gas for the powder. The powders were deposited on EN S235JR mild steel substrates with size 100x35x10 mm pre-heated at 200°C. Six tracks were deposited with 50% overlap. Welding parameters investigated are summarized in Table 4. Cross section of the cladded samples were checked for degree of bonding to the substrate, interface porosity and dilution from the substrate by using optical microscopy. The samples with good bonding to the substrate and dilution <10%, were selected for evaluation of the coating properties.

Test	Laser	Robot		
	Power [W]	Speed [mm/s]	Powder flow [g/min]	Comment
A	1500	16	20	Poor bonding to the substrate
B	2000	16	20	Good bonding, dilution <5%
C	2500	16	20	Good bonding, dilution approx 5-10%
D	1000	8	13	Poor bonding to the substrate
E	1500	8	13	Good bonding, dilution <5%
F	2000	8	13	Good bonding, dilution approx. 5-10%

Table 4. Laser cladding parameters used for coating of 100x35x10mm EN S235JR substrate, 6 overlapping tracks

- 5 Pucks with size 80x80x30 mm, pre-heated at 200°C were coated for production of abrasive wear test samples according to ASTM G65, procedure A. Two samples with size 58x25x30mm were cut out from each puck. The samples were then plane grinded to fulfil the requirements for the abrasive wear test.

Alloy	Power [W]	Speed [mm/s]	Powder flow [g/min]
6	1750	8	13
3	1750	8	13
4	1750	8	13
5	1750	8	13

Table 5. Laser cladding parameters used for coating of 80x80x30mm EN S235JR substrate

- 10 Furthermore, a laser cladding test with doubled travel speed was performed to assess the crack sensitivity of the alloy composition "Alloy 6" using the processing parameters for coating Alloy 6 onto an EN S235JR substrate size 80x80x30 mm as summarized in Table 6.

Alloy	Power [W]	Speed [mm/s]	Powder flow [g/min]
6	2000	16	20

Table 6. Laser cladding parameters used for cladding Alloy 6 on EN S235JR substrates, travel speed 16 mm/s

EVALUATION

The clads were investigated for presence of cracks and other surface flaws. They were cleaned (CRC Crick 110) and then coated with a red dye (CRC Crick 120) penetrating into surface defects or cracks through capillary forces. After 10 minutes excess dye was removed from the surface and a white developer (CRC Crick 130) applied. The developer drew the penetrant out of crevices, cracks or other hollow imperfections communicating with the surface and coloured them in red.

Rockwell hardness HRC was measured using a Wolpert Universal hardness tester. The coatings were ground. Seven hardness indents were performed on the flat surface and the average was calculated.

For measuring dilution from the substrate the coated samples were sectioned perpendicular to the coating direction and then ground on SiC paper. The cross section was examined using a stereomicroscope and dilution was determined geometrically. Prior to measurement, the samples were etched in Nital 1% to attack the substrate material and in this way facilitate the detection of the coating. The as-grinded coating cross section were photographed using a Leica stereomicroscope. The total coating area ($A_{coating} + A_{substrate}$) and the area of the coating that used to be substrate prior to overlay welding ($A_{substrate}$) were measured by image analysis. A dilution from substrate material by cross-sectional area was thus calculated as defined in the following equation:

$$\text{Dilution in \%} = ((A_{substrate}) / (A_{coating} + A_{substrate})) \times 100$$

For analysis of the coatings quality, microstructure and in some cases measurements of geometrical dilution from the substrate the samples were than moulded in Bakelite, ground and polished using standard procedures for metallographic sample preparation. Oxide polishing with colloidal SiO_2 was used as the final step of metallographic sample preparation. The coatings cross section was examined using a light optical microscope (Leica DM 6000) and a FEGSEM (Hitachi FU6600) equipped with a silicon drift detector (SDD) for EDS analysis (Quantax 800 Bruker). EDS maps for Mo and V were used to evaluate the volume fraction of phases present in the coatings by image analysis.

Low stress abrasive wear testing was performed according to ASTM G65 standard (ASTM G65: Standard Test Method for Measuring Abrasion Using the Dry Sand/Rubber Wheel Apparatus, 2010), procedure A, by using a commercial multiplex sand/wheel abrasion tribometer (Phoenix tribology TE 65). Five sample replicas per material were tested.

Impact wear testing was performed by using an in-house build test rig. A schematic of the set-up is shown in Fig.7. Standard steel bearing balls of mass m drop from pre-defined heights onto the coated test specimen. The potential energy (E_p) of each ball is $E_p = m h g$, wherein m is the mass of the ball, h is the drop height, and g is the gravitational constant. By varying the mass of the steel balls and the height from which they are dropped different potential energies i.e. impact energies are simulated. A data point corresponds to the total number of ball strikes for a pre-defined height, i.e. impact energy, until occurrence of a first circular crack around the impact dent. This type of model impact wear testing is suitable to rank impact wear resistance of materials exposed to impact overloads at relatively low impact velocities. Operation conditions closest to the modelling in this testing can be exemplified by a first contact of the excavator bucket teeth with the ground; by filling of the excavator buckets by the dig-out material; by forwarding the dig-out material to the truck bed etc. Abrasive wear is removed from this testing in difference to a combined abrasive-impact wear testing.

RESULTS

Dilution, abrasive wear resistance (AW) and hardness HRC of alloys 1-8 as processed into a hardfacing coating by PTA-welding and laser cladding are summarised in Table 7.

Alloy	PTA welding			Laser cladding		
	Dilution %	HRC	AW (mm ³)	Dilution %	HRC	AW (mm ³)
REF	<10	67	8.0	<5	67	9.0
1	7	67		<5	68	
2	7	67		<5	66	
3	6	66	8.9	<5	67	8.6
4	12	65		<5	66	7.8
5	<10	67	11.0	<5	66	9.3
6	10	62	13.0	<5	64	11.3
7	7	63		<5	62	
8	4	64		<5	61	

Table 7. Dilution, abrasive wear resistance and HRC of the alloys 1-8 as PTA welded and laser clad

In Alloys 1-8 with a Nickel content 3.5 wt.% to 6 wt.%, the abrasive wear resistance value is below 15mm³ and down to 8mm³ while hardness HRC ranges from 61 to 68HRC. This level of resistance to abrasive wear is comparable to NiSiB mixes with tungsten carbides, which are state of the art alloys in applications exposed to severe abrasive wear. This level of resistance to abrasive wear is also comparable to the reference alloy (REF). However, coatings based on a NiSiB matrix with tungsten carbides and coatings based on the reference alloy REF are known for being sensitive to crack formation.

By adequate additions of Nickel and Silicon according to embodiments of the present invention, a surprising improvement is achieved for the toughness and for the resistance to cracking of the iron-based alloy compositions when processed into a hardfacing coating without affecting hardness or abrasive wear resistance negatively. This is e.g. shown by the hardness and abrasive wear resistance data for the alloys in Table 7. Alloys with a Nickel content between 3 wt.% and 6 wt.% and a Silicon content above 0.2 wt.% show a good combination of hardness and abrasive wear combined with significantly improved resistance to cracking as illustrated in Fig. 1. While samples with low Nickel content (REF) and low Silicon content (Alloy 2) exhibit a pronounced tendency to crack formation, a combined increase in Nickel and Silicon significantly reduces the observed number of cracks (Alloys 3, 4, 8, M9, M10). A virtually crack free hardfacing coating is achieved for a Nickel content above 4 wt.% in combination with a Silicon content above 1 wt.% (Alloy 6), which reproducibly is surprisingly robust

against rapid melt pool cooling rates. This surprising robustness against variations in processing related parameters is further supported by hardfacing coating tests performed at doubled travel speed as illustrated in Fig.2. Fig.2 shows samples prepared using a travel speed of 16 mm/s (1m/min) and the coating parameters given in Table 6. An almost crack free coating is achieved despite the increase in travel speed from 8 mm/s to 16 mm/s.

The surprising improvement of the quality of the hardfacing coating is further supported by an analysis of the cross-section of laser cladded coatings made using such alloys as illustrated in Fig.6. Fig.6 shows cross-sectional LOM micrographs of coatings (bright material) applied by laser cladding onto a substrate material (grey material). The coatings shown in Fig.6 are made from Alloy 2 (Fig.6a), Alloy 4 (Fig.6b), and Alloy 6 (Fig.6c). Cracks and pores are seen as black defects in the bright coating material. A significant effect as to the reduction in pore defects as well as a reduction in the tendency to crack formation is observed as the Nickel content and the Silicon content are increased in agreement with the results on the coating quality derived from the above-mentioned die penetration tests. The coatings shown in Fig.6 are all prepared with a travel speed of 16 mm/s, a laser power setting of 2.5kW for alloy 2 and 4 and of 2.0kW for Alloy 6, and a feed rate of 20 g/min.

Impact resistance data is shown in Fig.8. Fig.8 shows the impact energy per strike as a function of the number of strikes needed to achieve the first crack in the coating. The graph shows data for the iron-based alloy compositions Alloy 3, Alloy 6, and the reference alloy REF. Each of the plotted lines is a linear regression to measurements obtained on at least two samples of the respective alloy, wherein measurement points have been collected for energies per strike of 30J, 25J, 20J, 15J, and 10J. The corresponding regression data are given in Table 10 below. The best performing samples may show a so-called run-out behaviour, where at the lowest impact energies per strike no crack formation is observed, or at least not observed in a reproducible manner, within a large number of strikes of up to 100 strikes. Data points showing such a run-out behaviour were not included in the linear regression. The diagram shows that for one and same impact energy the coatings made using alloy compositions Alloy 3 and Alloy 6 can withstand almost double impact energy before the first crack is formed when compared to the reference alloy (REF) with a Nickel content below 2 wt.%. Alloy

3 starts showing run-out behaviour below a strike-energy of 10J, while Alloy 6 starts showing run out behaviour below a strike-energy of 15J. For the reference alloy (REF) instead less than 20 strikes are sufficient to form the first crack when the impact energy is 10J.

5

One important insight underlying the present invention relies on an analysis of the microstructure of the alloys when processed by melting and subsequent cooling to form a (re-)solidified sample, as further explained by way of example below. The microstructure analysis reveals that the skilled person may use the present invention to design an alloy composition optimized for a particular application by setting the Nickel content of the iron-based alloy composition, and further adding Silicon within carefully selected ranges allowing for tuning the distribution of different phases in the microstructure of the processed material, in order to achieve desired properties of combined wear resistance including combinations of hardness, abrasive wear, impact wear, and/or coating quality (e.g. crack free / low porosity). Notably, Silicon was found to affect the amount of primary hard phase particles formed in the iron-based alloys with Ni additions, more particularly the amount of primary boride particles. A particularly advantageous range for the Silicon content for tuning the alloy properties was found to occur below 1.5 wt.%, or below 1.4 wt.%, or below 1.3 wt.%, or below 1.2 wt.%, or below 1.1 wt.%, or below 1 wt.%, and above 0.2 wt.%, or above 0.3 wt.%, or above 0.4 wt.%, or above 0.5 wt.%, or above 0.6 wt.%.

For a systematic implementation, the skilled person designing an alloy composition according to desired wear resistance properties may develop information on the phase formation properties of the alloy composition by producing a sample of processed alloy and analysing the microstructure of the sample with respect to its phase composition, and advantageously with respect to the fractions of primary boride particles and of eutectic matrix material in the processed alloy material. For the purposes of analysing different alloy compositions in a systematic implementation of the invention, the skilled person may e.g. prepare samples by melting the corresponding iron-based compositions and casting them into ingots that are polished for a microstructure analysis according to known metallurgical analysis techniques.

An example of such a microstructure analysis is given in the following. Alloys with a nominal Nickel content of 4 wt.% and a Si content varying between 0.2 wt.% to 2 wt.% were melted in an induction furnace and then poured in a copper mould. Chemical composition of the produced ingots was analysed and the results are reported in Table 1 as alloys 16, 17, 18, and 19. The microstructure was investigated using a SEM equipped with EDS detector for energy-dispersive X-ray spectroscopy.

Fig.3 shows the microstructure of alloys 16-19 as seen in SEM BSE (back scatter) micrographs, wherein alloy 16 has 0.2wt.% Si (Fig.3a); alloy 17 has 0.7wt.% Si (Fig.3b); alloy 18 has 1wt.% Si (Fig.3c); and alloy 19 has 2wt.% Si (Fig.3d). The microstructure of the ingots, shown in Fig.3 (Fig.3a-d), consists of primary dendritic carbides (PC, dark grey), primary borides (PB, white particles), eutectic structure consisting of Molybdenum rich borides and martensite as well as martensitic islands with possibly small amounts of retained austenite. An example of elemental mapping of B, C, Si, V, Mn, Fe, Ni, and Mo using EDS is shown in Fig.5 for alloy 19 with 2 wt.% Si.

Variations in the amount of primary borides (PB), eutectic structure (Eutectic) and martensite (Mart) with increased Si content is shown in Fig.4. The volume fraction of primary carbide is similar for all four alloys and approx. 17vol.%. The diagram shows that by increasing the amount of Si the volume fraction of primary borides (PB) and martensite (Mart) increases while the amount of eutectic structure decreases. Most notably, Silicon was found to influence the amount of primary hard phase particles formed in the iron-based alloy composition with Ni additions when varied within ranges below 2 wt.% of Si, with advantageous ranges as given above. A particularly pronounced response is seen in the range around and below 1 wt.% Si. The amount of primary borides as compared to the amount of eutectic matrix material affects the abrasive wear resistance of a clad. Controlling the Si content is therefore a most useful tool in determining the final microstructure of an alloy, and as a consequence the final properties of a clad. Similar results were obtained on PTA welded and laser clad-ded alloys as illustrated in Tables 8 and 9 for iron-based powder compositions of the type of the reference alloy REF modified with additions of Ni and Si.

Alloy	Ni wt.%	Si wt.%	PC vol.%	PB vol.%	Mart vol.%	Eutectic vol.%	AW (mm ³)
3	4	0.7	18	9	13	60	8.9
5	4	1.5	18	11	16	55	11.0

Table 8: Vol fraction of phases present in PTA welded alloys with different Si content and abrasive wear (AW) resistance

Alloy	Ni wt.%	Si wt.%	PC vol.%	PB vol.%	Mart vol.%	Eutectic vol.%	AW (mm ³)
4	4	1.0	19	10	14	58	7.8
6	5	1.5	18	13	13	55	11.3

Table 9: Vol fraction of phase present in Laser cladded alloys with different Si content and abrasive wear (AW) resistance

5

Alloy	Slope [J/strike]	Intercept [J/strike]	R ²
3	-0.79	31.2	0.95
6	-0.85	32.8	0.76
REF	-1.0	26.9	0.77

Table 10: Linear regression data for impact wear measurements using the ball drop method

CLAIMS

1. An iron-based alloy composition comprising
boron (B): 1.6-2.4 wt.%;
carbon (C): 1.7-3.0 wt.%;
5 molybdenum (Mo): 16. 0-19.5 wt.%;
nickel (Ni): 3.5-6.5 wt.%;
manganese (Mn): below 0.8 wt.%;
silicon (Si): 0.2-3.0 wt.%;
vanadium (V): 10.8-13.2 wt.%;
10 and balanced with iron (Fe).
2. The iron-based alloy composition according to claim 1, wherein the amount of silicon is 0.3-2.0 wt.%.
- 15 3. The iron-based alloy composition according to claims 1 or 2, wherein the amount of boron is 1.8-2.3 wt.%.
4. The iron-based alloy composition according to any one of claims 1 to 3, wherein the amount of nickel is 4.2-6.1 wt.%.
- 20 5. The iron-based alloy composition according to any one of claims 1 to 4, wherein a total amount of impurities in the iron-based alloy composition is below 1 wt.%.
6. The iron-based alloy composition according to any one of claims 1 to 5, wherein
25 the alloy composition is a powder composition.
7. The iron-based alloy composition according to claim 6, wherein at least 95 wt.% of the powder composition has a particle size of up to 300µm, or up to 250µm, or up to 200µm, or up to 150µm, and/or wherein at least 95 wt.% of the powder
30 composition has a particle size of at least 5µm, or at least 10µm, or at least 20µm, or at least 30µm, or at least 40µm, or at least 50µm.

8. An item comprising a substrate portion and a coating bonded to the substrate portion, wherein the coating is made using an iron-based alloy composition according to any one of claims 1 to 7 as a coating material.
- 5 9. The item according to claim 8, wherein the coating is applied by an overlay welding process, such as a plasma transfer arc (PTA) welding process or a laser cladding process.
- 10 10. The item according to any one of claims 8 to 9, wherein a substrate material dilution is below 20%, or below 15%, below 10%, or below 5%, or below 1%.
11. The item according to any one of claims 8 to 10, wherein the coating has a Rockwell hardness HRC of at least 60, at least 63, or at least 65.
- 15 12. The item according to any one of claims 8 to 11, wherein the coating has an abrasive wear resistance as determined according to ASTM G65, procedure A, of, below 15mm³, below 12mm³, or below 10mm³.
- 20 13. The item according to any one of claims 8 to 12, wherein the coating has an impact wear as determined according to the ball impact wear testing method of more than one strike for an impact energy per strike of 25J, more than 5 strikes for an impact energy per strike of 20J, more than 15 strikes for an impact energy per strike of 10J.
- 25 14. The item according to any one of claims 8 to 13, wherein the coating has a microstructure comprising primary boride and eutectic matrix, wherein a ratio of an amount of primary boride by volume to an amount of eutectic matrix by volume is below 0.3, or below 0.25.
- 30 15. Method of hardfacing a substrate, the method comprising the steps of:
 - providing a substrate;
 - applying a coating to the substrate using an iron-based alloy composition according to any one of claims 1 to 7 as a coating material.

16. Method according to claim 15, wherein the coating is applied by an overlay welding process, such as a plasma transfer arc welding process or a laser cladding process.

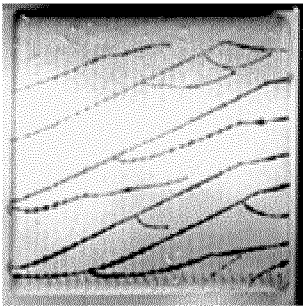
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1.5wt% Ni

4wt% Ni

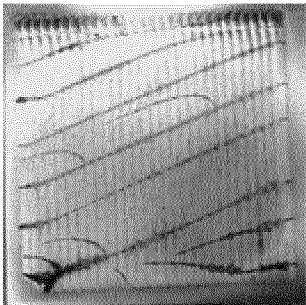
5wt% Ni

0.2wt% Si

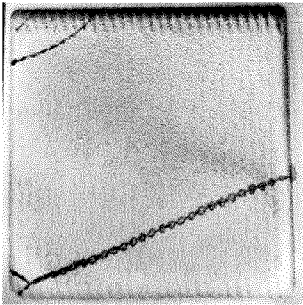


ALLOY 2

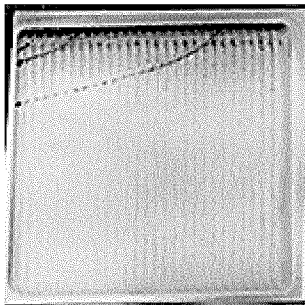
0.7wt% Si



REF

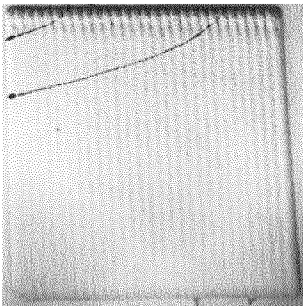


ALLOY 3

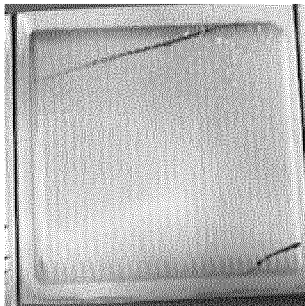


ALLOY 8

1wt% Si

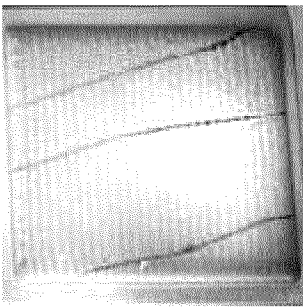


ALLOY 4

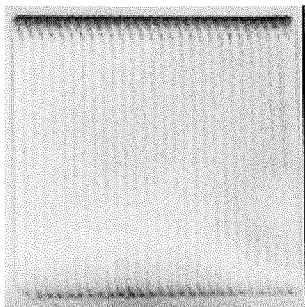


ALLOY M9

1.5wt% Si



ALLOY M10



ALLOY 6

Fig. 1

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ALLOY 6

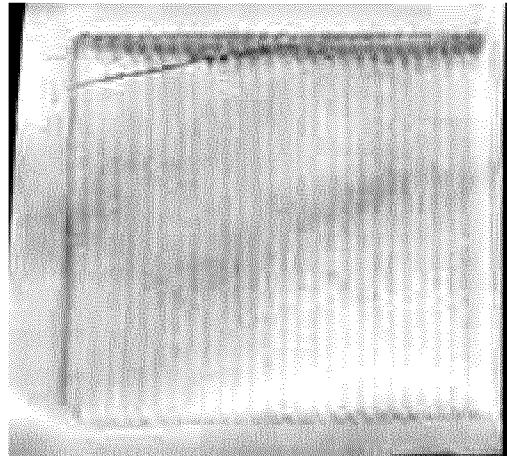
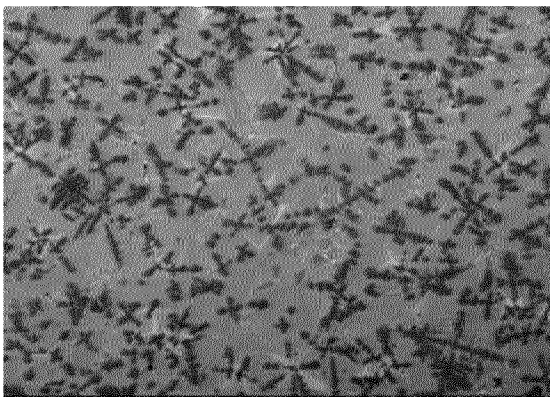
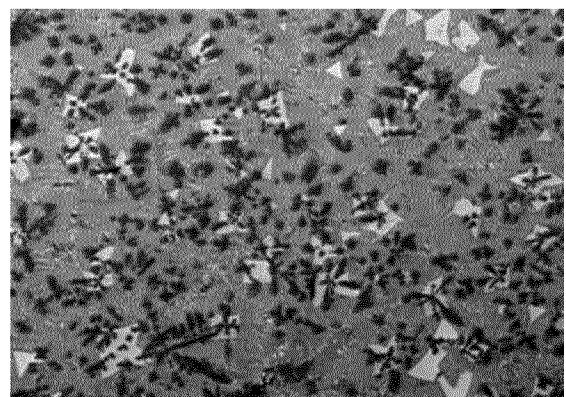


Fig. 2



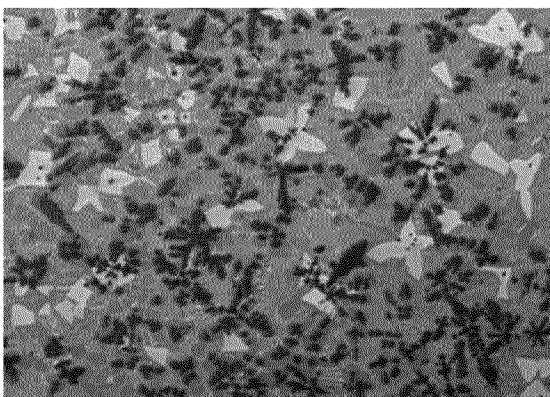
ALLOY 16, 0.2wt% Si 100μm

Fig. 3a



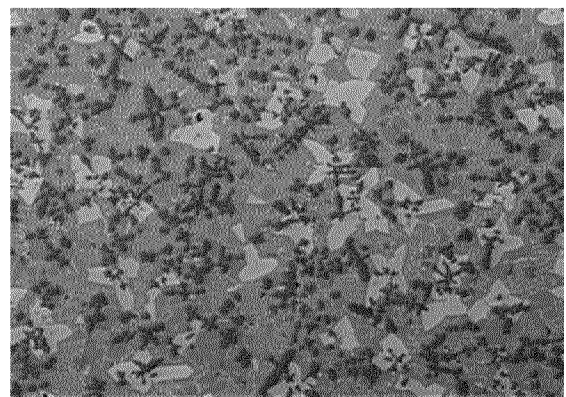
ALLOY 17, 0.7wt% Si 100μm

Fig. 3b



ALLOY 18, 1wt% Si 100μm

Fig. 3c



ALLOY 19, 2wt% Si 100μm

Fig. 3d

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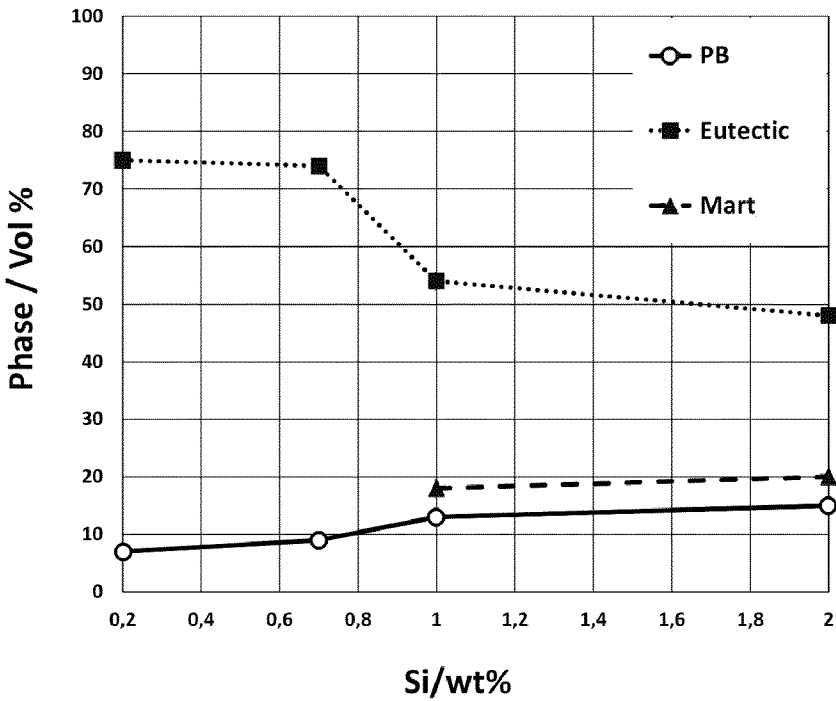
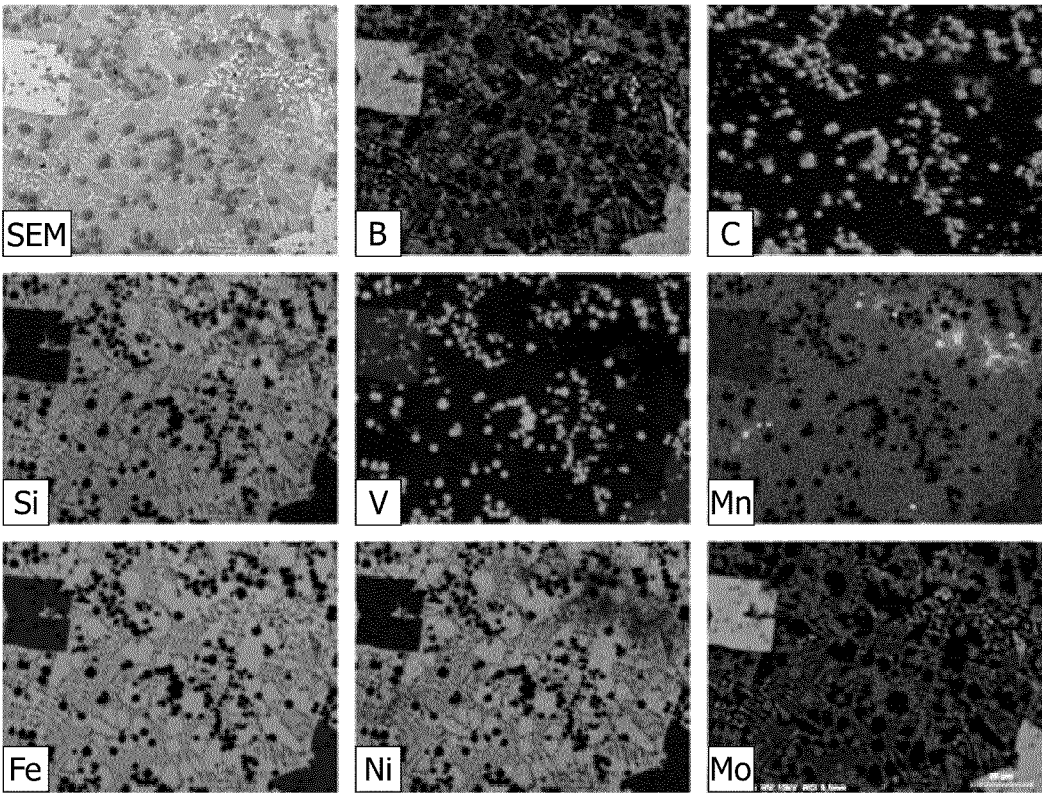


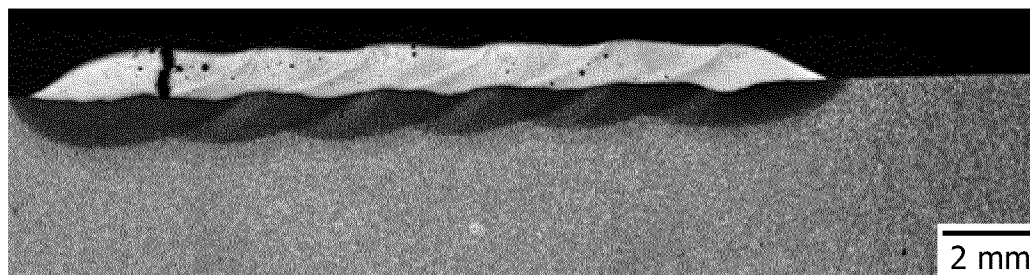
Fig. 4



ALLOY 19, 2 wt% Si

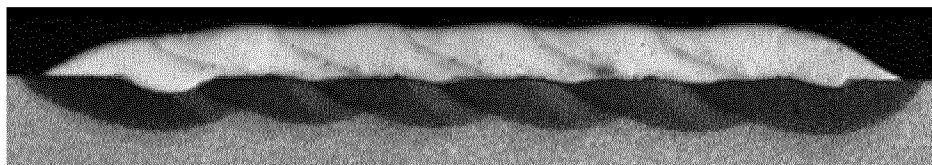
Fig. 5

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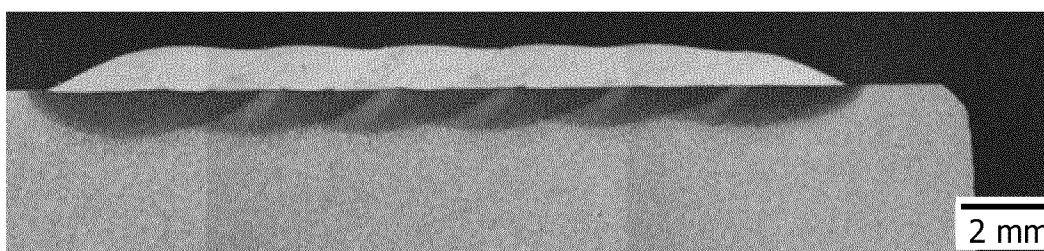
Alloy 2

Fig. 6a



Alloy 4

Fig. 6b



Alloy 6

Fig. 6c

5 / 5

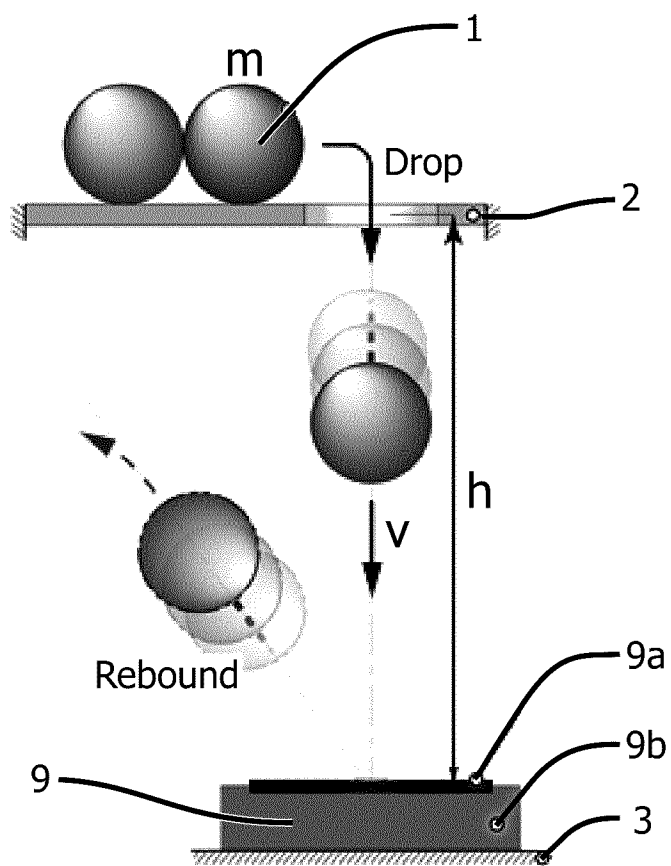


Fig. 7

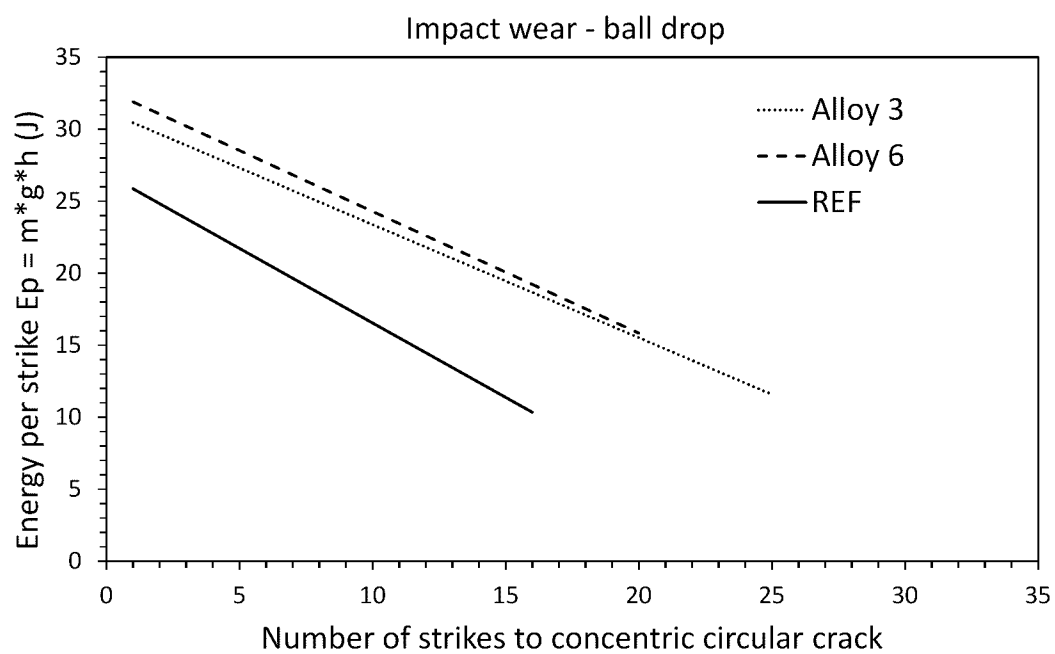


Fig. 8

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2019/066834

A. CLASSIFICATION OF SUBJECT MATTER

INV. B23K9/04 B23K10/02 C22C1/04 C22C38/02 C22C38/08
C22C38/12 B23K26/342

ADD.

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)

B23K C22C B22F

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2017/040775 A1 (SCOPERTA INC [US]) 9 March 2017 (2017-03-09) cited in the application examples P1,P2,P4; table 2 example 5; table 5	1-16
A	DE 195 08 947 A1 (PATENTSTELLE FUER DIE DEUTSCHE [DE]) 19 September 1996 (1996-09-19) claims 1-3	1-16



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

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"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

7 October 2019

Date of mailing of the international search report

17/10/2019

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Lilimpakis, Emmanuel

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2019/066834

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		AU 2016317860 A1	05-04-2018
		CA 2997367 A1	09-03-2017
		CN 108350528 A	31-07-2018
		EP 3344789 A1	11-07-2018
		JP 2018532880 A	08-11-2018
		US 2017066090 A1	09-03-2017
		US 2019160603 A1	30-05-2019
		WO 2017040775 A1	09-03-2017

DE 19508947	A1	19-09-1996	NONE
