Creation of corrosion resistant coatings on ductile iron by remelting flame sprayed layers using laser and electron beam

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Abstract. The paper presents the results of the research of the formation of thin surface corrosion resistant layers on ductile iron with spheroidal graphite. Surface layers were created by a two-step technological process. In a first step, the surface layer material was applied to the surface of the ductile iron by means of a flame-powder coating in a thickness of 0.8 to 1 mm. The treatment of the layer was carried out in the second step by means of a defocused laser beam or a programmed-deflected electron beam. The influence of the laser beam defocusing and the influence of the energy distribution of the deflected electron beam on the characteristics of the formed thin surface layer was studied. 40 mm thick GGG 40 ductile iron samples were used as the substrate experimental material. The Ni-B-Si-type nickel powder with the designation NP22 and Ni-Cr-B-Si-type nickel powders of the type NP52 were used to form the surface layer. The quality of layers was assessed on the basis of surface forming, metallographic evaluation of selected properties of the layer and measurement of microhardness at the interface of the layer and the substrate material.

1. Introduction
In modern history, the first ductile cast iron was produced in 1934, but its broader industrial use is dated from the discovery of possibility of its modification by magnesium in master alloy with nickel in 1942.[1]. Extremely good mechanical properties, good workability and relatively low price per kilogramme are the most important reasons for a broad use of ductile cast irons in industry. An alloy with graphite in the form of globules is characterised by a strength of 400 MPa and has approximately 10% lower density in comparison with cast steel. It is used mainly in the automotive and mechanical engineering industry. As the nuclear energy industry was developing, it also became widely used in the production of heavy thick-walled castings – transport and storage containers for spent nuclear fuel [2-5]. Due to a relatively low corrosion resistance of ductile cast iron, the need for a significant increase of its corrosion resistance arises. One of the solutions to this problem is creating a thin surface layer on functional and contact surfaces of the container. General requirements for surface finishing of functional surfaces of a cast iron container intended for use in nuclear energy industry are as follows:

- High corrosion resistance.
- Provision of surface decontamination (dependent on surface porosity).
- Heat resistance of the layer ca. up to 300°C.
- Stability in radioactive environment.
- Resistance to potential damage during handling.
- Homogeneity of the layer also after metalworking without through discontinuities.
- Guaranteed cohesion with the base material.
- Repairability.
Inertness to a boric acid solution in the case of wet storage of spent nuclear fuel. Similarly to surface finishing of other metallic materials, arc and beam technologies are applied to cast iron in creating thin, corrosion resistant surface layers. However, the problematic weldability of cast iron prevents practical applicability of these technologies. The greatest obstacle is a high content of carbon, which causes the thermally affected area to be prone to opacification. Also, the situation is complicated due to the ability of solidification of cast iron according to Fe-Fe3C metastable system, when C is in the structure in the form of ledeburite and cementite, which can have a significant impact on the solidity of the created layer [1, 2]. The objective of the presented experimental tests was to design and verify the technology of creating thin corrosion resistant layers on the ductile cast iron with globular graphite by applying remelting of sprayed flame-powder layers using laser and electron-beam technologies.

2. Problem analysis
Nowadays patented methods of electrolytic metallic coating are used for creating functional surface layers on cast irons. The created layers are corrosion resistant and relatively easily decontaminable. However, they possess low resistance to mechanical damage. The methods of creating layers of required properties on cast irons with globular graphite using welding technologies have significant difficulties. The requirements connected with reaching high level of adherence of the layer to the base material and with resistance of the layer to deterioration demand creation of a good metallurgical bond between the layer and the base material. On the other hand, the requirement for a good corrosion resistance poses challenges for a low level of blending the material of the layer with the base material.

Due to the high carbon content, the base material (ductile graphitic cast iron) requires a specific heat mode in the process of surfacing. There is an opinion accepted by professionals that during surfacing of cast iron using arc technologies, application of pre-heating and post-heating is required, with the aim to lower the steepness of thermal gradients and provide solidification of the cast iron according to the stable system (Fe – graphite). The possibility to use arc methods for creating corrosion resistant and decontaminable layers on the ductile cast iron was researched in numerous works [2,5]. Several noteworthy results were achieved within the research. For example, the use of TIG pulse mode with pulse frequency in the order of hundreds Hz enabled to create solid single-layer- or multiple-layer claddings with nickel-based additive material without the need to apply pre-heating and/or post-heating. The disadvantages are proneness to cracking as well as low productivity [4].

It appears that application of beam technologies, such as laser and electron beam, is a suitable technological solution. The main assumption for the use of beam technologies is the fact that they have sufficient power to create a metallurgical bond at the interface of the layer with the base material. They enable to create 2D heat fields by defocusing of a laser beam or electron beam and create conditions for minimum blending of the base material with the material of the layer. In addition, during application of electron beam, we can perform the process in vacuum that provides perfect protection of the process against oxidation and also enables degassing of the fused layer. By using a programmable biaxial deflection of electron beam, the conditions for optimisation of areal distribution of beam energy in the process of sprayed layer processing are created [6].

3. Experimental material
The claddings were executed on test samples with the dimensions of 100 x 100 x 40. The samples were made of GGG 40 alloy type with globular graphite. Following technologies were used:
1) Remelting of the sprayed flame-powder layer by defocused laser beam.
2) Remelting of the sprayed flame-powder layer by programmed electron beam deflection.

The quality of layers or claddings was assessed based on:
- Visual inspection of surface formation of the cladding.
- Metallographic inspection of integrity and structure on cross sections of claddings (base metal – transition layer – cladding). The samples of cross sections of claddings were mechanically ground and polished, and etched for improving the contrast of the structure. The observation
was performed using an OLYMPUS GX 51 light microscope equipped by an ARTCAM 300MI digital CCD camera.

- Micro-hardness measurements – at the interface of the cladding testify to the character of bond and size of blending of the filler material with the base. The test was performed according to STN EN 1043-2 with a load of 100 p and a load time of 10 s. Micro-hardness was measured by a Haneman micro-hardness meter connected to a NEOPHOT2 metallographic microscope.

- The IPG YLR 4500 solid-state fibre laser with the maximum output power up to 4.5 kW was used as a laser source. The laser beam was transported to the PRECITEC YW50 welding technological head using optical fibre with a diameter of 0.3 mm. The focal length of the focusing lens was 200 mm. Protection of surface in laser remelting was provided by an inert gas.

- As a source of electron beam, the PZ EZ ZH4 electron-beam welding device was used, with the power of electron beam up to 15 kW and accelerating voltage of 60 kV, equipped by a system of dynamic biaxial deflection of PZ DF 5 type.

In laser remelting of the spraying, a defocused laser beam with a wave length of 1.06 µm was used. The IPG YLR 4500 solid-state fibre laser with the maximum output power up to 4.5 kW was used as a laser radiation source. The laser beam was transported to the PRECITEC YW50 welding technological head using optical fibre with a diameter of 0.3 mm. The focal length of the focusing lens was 200 mm. During the processing, the focus of laser beam was set in the distance from +40 to +60 mm above the sample surface, which ensured the beam defocusing. By laser beam defocusing, the beam energy concentration is changing and the energy interacts with the sprayed powder layer. Protection of surface in laser remelting was provided by an inert gas. NP 22 powder was used in the laser experiments.

In electron-beam processing, the remelting of the spraying was performed on the PZ EZ EZ4 electron-beam welding device was used, with the power of electron beam up to 30 kW and accelerating voltage of 60 kV. The PZ DF 5 system intended for programmed dynamic biaxial deflection was used for remelting. The biaxial, computer-controlled deflection system enabled to change the area distribution of electron beam by programme. An advantage of electron beam is the fact that the remelting process is carried out in the high vacuum environment, which prevents oxidation, while ensuring good degassing with the effect of decreasing porosity of the remelted layer. A disadvantage is the need of creating a vacuum environment, which may increase the expenses per area unit of cladding creation.

The principles of surface processing of the layer applied to the surface of the base material by the technology of flame-powder spraying are depicted on figures 1 and 2. The areal distribution of laser beam energy has a static Gaussian distribution. On the other hand, the PZ DF5 programmable system of electron beam deflection enables the beam deflection in the angle of ±7° in the latitudinal and also longitudinal direction to the surfacing movement. The maximum frequency in both deflection axes is
15 000 Hz. By programming the deflection system, we influence the electron beam energy distribution upon the surface layer, i.e. in the processing of the layer. The system enables to reach a constant energy density during the layer processing or any course of beam energy density based on programme commands.

4. Experimental material

4.1. Base material
Cast iron GGG 40
Ductile cast iron (EN-GJS-400-18) is ferritic with C in the form graphite globules with a minimum tensile strength of 400 MPa. It features high shock resistance and relatively good thermal conductivity. The reference chemical composition of the alloy is specified in Table 1.

| Table 1. Chemical composition of cast iron GGG 40 in wt. % |
|--------|--------|--------|--------|--------|--------|
| C      | Si     | Mn     | S      | P      | Mg     |
| 3.4 – 3.6 | 2.5 – 2.7 | Max. 0.2 | Max. 0.01 | Max. 0.05 | 0.03 – 0.08 |

4.2. Material of applied layer
NP 22 powder
Ni-B-Si-based nickel powder marked as NP22 was used for flame-powder spraying. The NP 22 powder is slag-forming, intended for thermal spraying. The particles have a spherical shape and size of 45 – 90 µm. The melting temperature of NP 22 powder is 1 100 °C and the applied layer reaches hardness of 18 – 24 HRC. The applied layer is corrosive resistant, abrasion resistant and well machinable. The reference chemical composition of NP 22 alloy is specified in Table 2.

| Table 2. Chemical composition of powder NP 22 in wt. % |
|--------|--------|--------|--------|--------|
| C      | Si     | B      | Fe     | Ni     |
| Max. 0.25 | Max. 5.0 | Max. 3.0 | Max. 5.0 | Rest. |

NP 52 powder
Ni-B-Si-Cr-based nickel powder was used for flame-powder spraying. The NP 52 powder is slag-forming, intended for thermal spraying. The particles have a spherical shape and size of 45 – 90 µm. The melting temperature of NP 52 powder is 1 000 – 1 100 °C and the applied layer reaches hardness of 50 – 54 HRC. The applied layer is flame and corrosive resistant and well machinable. The reference chemical composition of NP 52 alloy is specified in Table 3.

| Table 3. Chemical composition of powder NP 52 in wt. % |
|--------|--------|--------|--------|--------|--------|
| C      | Si     | B      | Fe     | Cr     | Ni     |
| Max. 0.4 | Max. 5.0 | Max. 3.0 | Max. 5.0 | Max. 11.0 | Rest. |

5. Experimental results

5.1. Laser remelting of flame-powder spraying
Within the experimental works carried out, the possibility of two-stage creation of surface layer with special properties on the ductile cast iron. A layer of Ni-based powder (NP 22, NP 52) was applied to the base material using the flame-powder technology. The thickness of the spraying was 0.8 – 1.2 mm. The structure of the sprayed layer is characterised by a relatively high porosity and a highly rough surface, which hinders the possibility of decontamination or makes it impossible, and lowers the corrosion resistance. Figure 3 depicts the surface of the sprayed layer and Table 4 presents the results
of areal semi-quantitative analysis of presence of the most important alloying elements of the layer, sprayed by flame-powder spraying. The layer was sprayed by NP 52 nickel powder. The areal EDX analysis results show that the chemical composition corresponds to the reference chemical composition of the powder used. The measured value of the C content is distorted with errors caused by possible contamination with organic compounds during manipulation and preparation of the sample. The issues of the EDX method in measurement of the content of light atoms is next source of the errors.

Table 4. Results of areal EDX analysis of the spray layer

|       | C   | Al  | Si  | Ca  | Cr  | Fe  | Ni  | Total |
|-------|-----|-----|-----|-----|-----|-----|-----|-------|
| Spectrum | 29.58 | 1.02 | 3.38 | 0.59 | 10.13 | 7.16 | 48.14 | 100   |

The measured results point out the fact that the properties of the sprayed layer do not comply with the requirements for corrosion resistance and decontaminability. For this reason, the surface layer was further processed by remelting by laser and electron beam.

In the process of remelting by laser, a defocused laser beam that enables creation of a wider laser beam spot. The defocusing parameters were defined in a way that the laser beam focus was in the distance of +40mm, +50 mm and +60mm above the layer surface. NP 22 nickel powder was used as layer material. With the laser beam power of 4.5 kW, we defined the defocusing value of +50 mm above the surface of sprayed layer as optimum. The width of the laser beam spot was 9 mm. The parameters of processing (remelting) are specified in Table 5. Surface of the remelted layer was smooth without visible surface pores or non-integrities (figure 3).

Table 5. Results of areal EDX analysis of the spray layer

| N.o | Laser beam power, kW | Velocity, mm/s | Focal position | Shielding gas flow rate, l/min |
|-----|----------------------|----------------|----------------|-------------------------------|
| 1.  | 4.5                  | 7              | + 50           | 15, He                       |
| 2.  | 4.5                  | 5              | + 50           | 15, He                       |
| 3.  | 4.5                  | 5              | + 50           | 15, He                       |
| 4.  | 4.5                  | 5              | + 50           | 15, He                       |

Figure 3. Surface of remelt runs made by defocused laser beam.

Since the powder contains a flux, a thin, inconsistent layer of slag was created on the surface of the cladding. Inconsistent distribution of energy in the beam was eliminated by applying a change of overlapping of individual weld beads.

A cross section of the remelted layer (NP 22) together with the details of individual cladding areas are depicted in Figure 4. Remelting of the powder spraying is not even throughout the width. The size
of the fused area of the alloy is dependent on geometry of the defocused beam and thickness of the applied layer. The presence of closed pores was found in the cladding after remelting. It is possible to see a sintered character of an insufficiently remelted surface layer in the overlapping areas. By optimising the size of overlapping of individual trajectories of layer processing, it is possible to reach the required quasi-homogeneous densification of the sprayed layer with the good metallurgic bond with the base material.

![Figure 4. Structure on cross-sections of laser remelted layer](image)

The micro-hardness measurement results are specified in Figure 5. The fusion line showed a moderate undulation. The depth of penetration of the melted material into the base material reached the value up to 200 µm. The hardness in the area of moderate blending ranged from 230 to 956 HV 0.1. The undulation of the interface is caused by the presence of graphitic nodules that melt down due to heat mode, which leads to creation of a eutectic with an increased hardness of 839 – 956 HV 0.1. In the heat-affected zone, during the heating beyond the austenitisation temperature, carbon saturation of the matrix around the graphite nodules occurred. In the subsequent cooling, the cooling velocity prevented a complete reverse diffusion of carbon into the graphitic particles and led to pearlite transformation.

In the transition areas where the beam energy was only enough for a only sintering of the powder, the undulation of the fusion border is lower and the creation of a eutectic was suppressed, which is proved by results of metallographic observation.
5.2. *Electron beam processing (remelting) of flame-powder spraying*

A similar procedure of remelting of the sprayed layer was selected in the case of using electron beam. Electromagnetic biaxial computer-controlled deflection of electron beam was used for homogenisation of energy distribution in the beam spot. The remelting parameters are specified in Table 6.

**Table 6.** Electron beam remelting parameters

| Process | Deflection |
|---------|------------|
| Voltage, kV | Beam current, mA | Velocity, mm/s | Ch. A | Ch. B |
| 55 | 60 | 5 | linear | Linear |
|     |     |     | 358 mV | 3 583 mV |
|     |     |     | 30 Hz | 1.5 kHz |

**Figure 5.** Micro-hardness at the interface cast iron GGG 40 – laser remelted layer (NP22 powder).

**Figure 6.** Surface of electron beam processed NP22 powder layer.
In the experiments, the samples of GGG 40 alloy sprayed by NP 22 and NP 52 nickel powders were used. Based on the visual assessment, the surface of the remelted layer was moderately undulating with excessive trace edges due to the melt pool dynamics during deflection (Figure 6). A moderate spatter on the surface of the claddings was observed as well.

A low blending of the welded layer with the base also resulted in lower values of micro-hardness in the fused area of the alloy (Figure 7). The structure of the remelted area was similar to the structure when using laser beam.

An areal energy – disperse analysis of the remelted powder spraying was created. depicts the surface formation of the sprayed layer of NP 52 powder and Table 7 presents the results of areal semi-quantitative analysis of presence of the most important metal parts of the layer. The EDX analysis results show that the chemical composition corresponds to the chemical composition of the powder used.

**Table 7.** Results of surface EDX analysis of electron beam melted (NP52) layer

|     | C   | Si  | Cr  | Fe  | Ni  | Total |
|-----|-----|-----|-----|-----|-----|-------|
| Spectrum | 18.05 | 5.39 | 8.95 | 5.04 | 62.57 | 100   |

Figure 8 depicts the results of micro-hardness measurement. The hardness ranged from 272 to 667 HV$_{0.1}$. Due to a lower course velocity of remelting and areal deflection of the beam, a higher amount of heat was taken into the material, which led to lowering of the tendency to create hard structures in comparison with laser processing.
6. Conclusion
The objective of the submitted article is to present the possibilities of creating thin surface corrosion resistant layers on GGG 40 ductile cast iron with the use of beam technologies. Within the experimental research, the properties of the surface layers created by a two-stage technology using nickel-based powders were studied. A flame-powder spraying with the thickness of ca. 1 mm on the ductile cast iron was remelted by electron or laser beam. Experimental research brought following results:

- Surface layers remelted by laser as well as electron beam showed compact and without significant of surface.
- The physical principle of beam technologies enables precise regulation of energy density of the technological process. In comparison with other heat sources, it enables minimum impact on the welded base material.
- The surface of the remelted layer by electron beam was undulating due to the influence of the melting bath dynamics in rasterising, which may be suppressed by optimisation of pattern and parameters of electromagnetic deflection.
- A limitation of beam technologies is the size of thickness of the remelted layer per one pass. It was verified that an optimal thickness of the remelted layer in the fusion process of the ductile cast iron is within the range of 0.8 – 1 mm. In case of a greater thickness, the heat effect of the beam is insufficient for its complete remelting and a part of the layer remains sintered.
- The structure of the ductile cast iron influences the properties of the created layer. If graphite is not in the form of globules, but in the form of irregular shapes, a probability of more intensive dissolution of such particles increases, which raises the risk of formation of undesirable fragile and hard structures.

Based on the results of the presented research, we may state that application of beam technologies in the creation of corrosive resistant and decontaminable layers on ductile cast iron does not require pre-heating. To reach a solid cladding without the use of pre-heating, it is important to effectively dose the energy into the cladding process together with an appropriate selection of filler material composition (without carmine-forming elements, Cr, B) and thereby positively influence the heat-affected zone microstructure and/or minimise the amount of hard and fragile structures.

7. Acknowledgments
This research was supported by the Slovak Research and Development Agency based on Contract No. APVV-17-0432 as well as by the project of industrial research of the Ministry of Education, Science, Research and Sport within the call Stimuly 2018 based on Contract Reg. No. 1227/2018.

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