# Manufacturing technologies thick-layer coatings on various substrates and manufacturing gradient materials using powders of metals, their alloys and ceramics

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### ABSTRACT

**Purpose:** The paper is a comprehensive review of the literature on manufacturing technologies thick-layer coatings on various substrates and manufacturing gradient materials using powders of metals, their alloys and ceramics.

**Design/methodology/approach:** Extensive literature studies on manufacturing technologies thick-layer coatings on various substrates and manufacturing gradient materials using powders of metals, their alloys and ceramics have been carried out. The paper is illustrated with examples of various structure images obtained as part of research of engineering materials made by authors with powders. By using knowledge engineering methods, development perspectives of individual technologies were indicated.

**Findings:** The manufacturing technologies thick-layer coatings on various substrates and manufacturing gradient materials using powders of metals, their alloys and ceramics as the advanced digital production (ADP) technologies are proves the highest possible potential and relatively good attractiveness, as well as their fully exploited attractiveness or substantial development opportunities in this respect.

**Originality/value:** According to augmented holistic Industry 4.0 model, many materials processing technologies and among them manufacturing technologies thick-layer coatings on various substrates and manufacturing gradient materials using powders of metals, their alloys and ceramics are becoming very important among product manufacturing technologies. They are an essential part of powder engineering.

**Keywords:** Powder engineering, Manufacturing of powder products, Manufacturing technologies thick-layer coatings using powders, Dendrological matrix of the technologies potential and attractiveness, Holistic augmented Industry 4.0 model

MANUFACTURING AND PROCESSING

## 1. Introduction

The paper [1] presents a general classification of technologies and methods of additive manufacturing (Fig. 1) in which metals and their alloys powders and engineering ceramics powders are used. In the cited article [1] all the mentioned groups of technologies are discussed except for the layer powder deposition methods, which are the subject of this paper. Application of thick-layer coatings to surfaces of substrates made with various ways gives extensive possibilities of using powders of metals and their alloys and ceramic materials. For substrates, manu-facturing methods are used, including casting, plastic deformation of alloys manufactured by conventional metallurgy methods, as well as powder metallurgy methods and through additive technologies. Its approach can always be considered as part of unique hybrid technology for the production of finished products, although finishing treatment is almost always necessary. The main goals of this activity, most often synergistically and jointly, is the final formation of a geometric form, ensuring selected properties of the surface layer, as well as the manufacturing of composite and/or gradient materials required due to the designed utility functions of products. These issues are the subject of numerous publications of the authors [2-52].

Using the procedural benchmarking method and the universal scale of relative states at work [53], a rating of the analysed manufacturing technologies thick-layer coatings on various substrates and manufacturing gradient materials using powders of metals, their alloys and ceramics among other powder engineering technologies was made. Figure 2 presents the dendrological matrix of manufacturing techno-logies thick-layer coatings on various substrates and manufacturing gradient materials using powders of metals, their alloys and ceramics showing the technology rating due to their attractiveness and potential. Manufacturing technologies thick-layer coatings on various substrates and manufacturing gradient materials using powders of metals, their alloys and ceramics analysed in this paper are summarised in Table 1 with the markings given in Figure 2.
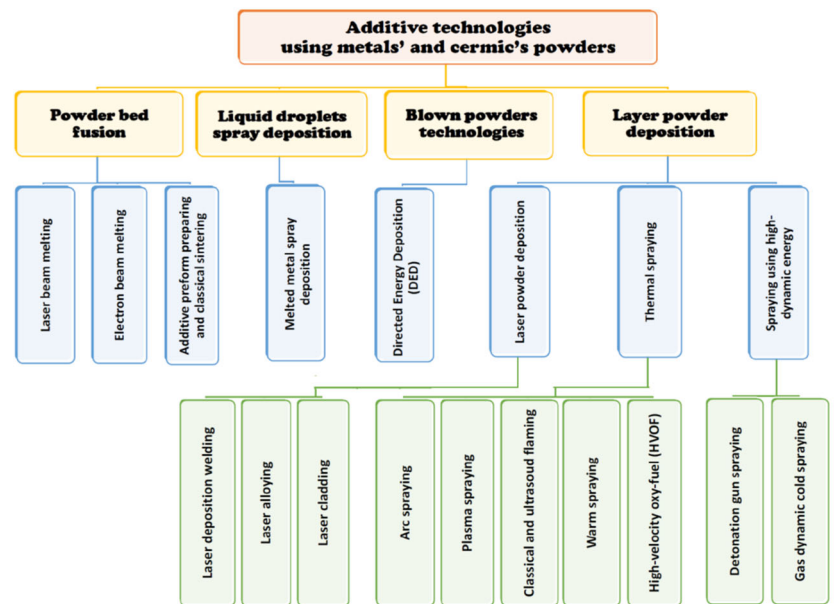


Fig. 1. The general classification of technologies and methods of additive manufacturing in which powders of metals and their alloys and engineering ceramics powders are used

The best positions were obtained by electron beam powder deposition, detonation gun spraying and laser alloying/feeding, which are becoming more and more popular, allowing the application of permanent coatings using modern equipment with even better performance and environmental friendliness.

The group, as mentioned earlier of technologies constitutes a significant scope of powder engineering discussed in the series of papers [1,53,54] in which this paper is the last in turn. In [4, 55-57], assumptions and the concept of development of subsequent stages of the industrial revolution are presented, with emphasis on the importance of information technologies, including cyber-physical systems CPS. A unique role was assigned to them in additive technologies that would be uncompetitive to all other manufacturing technologies. Further development at the current stage of Industry 4.0 would depend on them. In authors' r own works [6,23,25, 58-60] it was pointed out that the industry 4.0 model presented in [4, 55-57] requires augmentation, as the development of industry equally depends on cyber-IT components, development of materials,

Table 1.
Analysing manufacturing technologies thick-layer coatings on various substrates and manufacturing gradient materials using powders of metals, their alloys and ceramics

| Surface layers deposition technologies | | | |
|---|---|---|---|
| AS | Arc spraying | FS | Flame spraying |
| CC | Conventional cladding | GPMAC | Gas powder metal arc cladding |
| DGS | Detonation gun spraying | HVOF | High-velocity oxy-fuel |
| EBPD | Electron beam powder deposition | LAF | Laser alloying/feeding |
| FC | Flame cladding | LC | Laser cladding |
| FGMM | Functional gradient materials manufacturing | PC | Plasma cladding |
| | | PS | Plasma spraying |

manufacturing technologies and machines. In this context, the importance of powder engineering technology is crucial, as demonstrated in all papers of this cycle. 4.0.

## 2. General characteristics of spraying methods of manufacturing technologies thick-layer coatings on various substrates using powders of metals, their alloys and ceramics

A large group of these methods are spraying methods in which solid particles are applied to the surfaces of other materials. If the substrate does not melt when using the surface layer, the process is thermal spraying, and the connection is purely mechanical, with partial diffusion. A thermal spray is a group of methods in which molten or pasty coating material is applied to the surface of a previously prepared substrate. Most of the other methods in this group can be included in welding technologies due to the phenomena that accompany them, and in essence, they are all additive. The issue has a very extensive bibliography and is widely discussed in the own review papers of the authors of this paper [61-67].

A technology that can be classified as additive manufacturing and thick-layer coating technology at the same time is previously discussed direct energy deposition, also called laser metal deposition LMD. In this process, a nozzle mounted on multi-axis arm deposits molten material onto a specific surface on which it solidifies. If the three-dimensional element is constituted from scratch on a working platform, the technology should undoubtedly be included in additive manufacturing. However, if the technology serves the application of surface
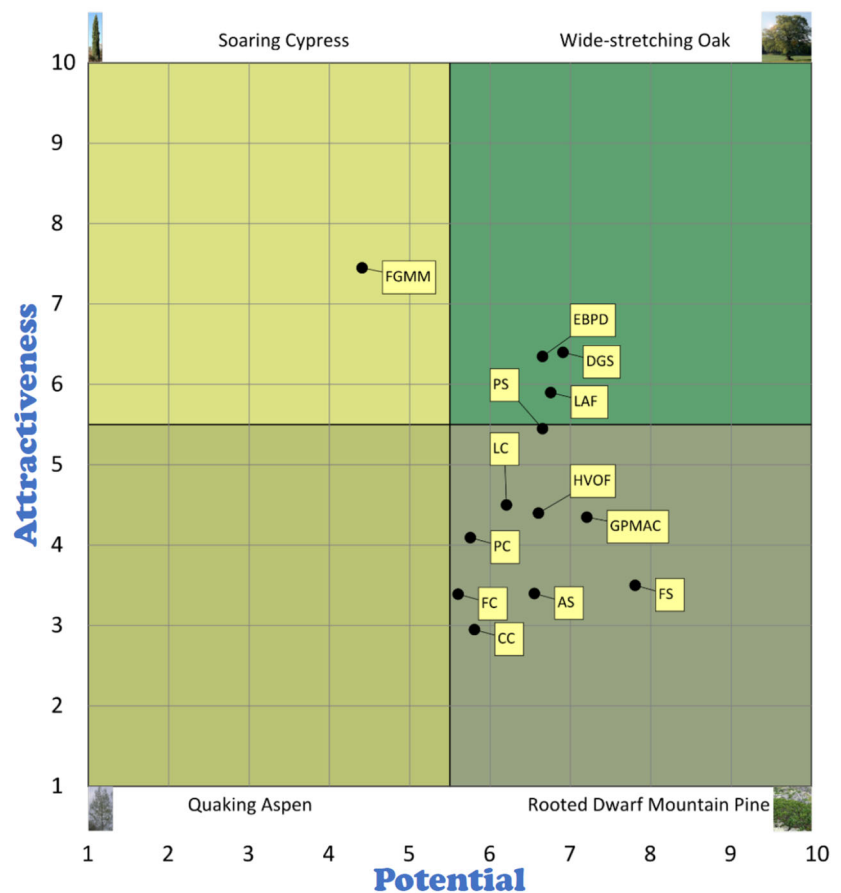


Fig 2. Dendrological matrix manufacturing technologies thick-layer coatings on various substrates and manufacturing gradient materials using powders of metals, their alloys and ceramics

layers on a substrate produced by other methods or similar but in different technological processes, it should be qualified to the currently discussed group of technologies using powders of metals, their alloys and ceramic materials. Often LMD is used as repair technology.

Powders (including unalloyed, low-alloy and high-alloy steels, high-alloy cast iron, cobalt, nickel, copper alloys, corrosion-resistant steels, ceramic, cermets and heat-resistant

carbides, oxides, borides and silicides, except for polymeric materials that do not fall within the scope interests of this paper) can be applied in layers on the surface or edge of the substrate material with different chemical composition by welding methods. Usually, this improves abrasion, erosion, thermal or chemical wear resistance without having to have a large enough element made of expensive material or challenging to manufacture, or without the required properties in the entire volume. As a result, surface layers with tenths of a millimetre to several millimetres thick are obtained, which show increased utility properties, high hardness, and high resistance to abrasive wear and thermal fatigue.

Thermal and detonation spraying of surface layers is a primary group of technologies that determine the essence of thick-layer coatings using powders of metals, their alloys and ceramic materials on substrates made by various methods. It is not essential for this qualification of the method whether the material used is a powder produced by the typical methods described previously, e.g. by atomization, or whether the preparation of the powder is an autonomous part of thermal or detonation spraying, and the input material is wires, tapes or materials in another form. Regardless, the material always gets onto the substrate in the form of spray powder and it is deposited on the surface of the element or product on which it solidifies.

Thermal spraying processes are widely used [64], including for protective coatings, aluminium or modified on an aluminium basis, such as Al-Si, Al-Cr, Al-Pt, Pt-Al-Cr. They allow increasing the maximum operating temperature above 1100°C, in which the requirements of appropriate properties are met by directional crystallized Ni alloys and single crystals. The development of materials for gas turbine components is primarily determined by increasing the operating temperature. Further possibilities of increasing the operating temperature by modifying the chemical composition of alloys or the technology of obtaining elements are increasingly limited. Coatings generally described as MeCrAlY, where Me could be Co, Ni, NiCo, as well as CoNiCrAlYHfSi and CoCrAlYSi, as well as thermal barrier coatings (TBC), forming thermal insulation protecting the alloy against high temperature. The material for these coatings is $ZrO_2$-$Y_2O_3$ or $Al_2O_3$, $Al_2O_3$ + 5% Ni, and Me-CrAl coatings are used as the interlayer. The type and morphology of the layers affect the fatigue life of nickel alloys with coatings to varying degrees. Adhesive-diffusion layers behave most preferably.

The costs of thermal flame spraying are much higher than plasma spraying, while the plasma spraying production line is much more expensive than flame spraying devices.

In [68], based on the literature data, a comparison of the characteristics of various thermal spraying technologies is presented (Tab. 2).

In this context, among the technologies listed in the technology platform of the augmented holistic model of Industry 4.0 [23,59] there is a wide set of technologies using powders of metals and metal alloys or their mixtures with non-metallic powders to obtain semi-finished products and products from these powders in a solid-state without the need to melt the main component. Often, these technologies are used to manufacture finished products or prefabricated elements with geometric features very similar to the final shape required, and for shaping their structure and physical and chemical properties. Such products can be used directly or can be subjected to finishing subtractive manufacturing. The assumption made by the authors of this paper is to break the stereotype that the issue is limited to powder metallurgy, although its essential role in this respect is absolutely irrefutable. However, as demonstrated in the content of that paper, the issue is immeasurably broader and more complex. Many times it does not only apply to metals and their alloys, but also to composite materials with the participation of metals as well as ceramic materials, which for semantic reasons is difficult to include in metallurgy. It is a much broader context of material engineering. This was noted, although the fundamental premise for all classifications and subsequent analyses was the powder form of the input materials used. The incorporation of polymer and composite materials with their participation was systematically avoided. Including this topic would probably have to extend the paper twice.

Table 2.
Comparison of the characteristics of various thermal spraying technologies

| Technology | Source of heat | Process temperature, °C | Deposited material | Velocity of impacting particles, m/s | Adhesivity | Efficiency, kg/h |
|---|---|---|---|---|---|---|
| Arc spraying | Electric arc | 5000–6000 | Metals | 250 | ◑ | 30 |
| Plasma spraying | | 8000–20,000 | All | 250–1200 | ◑ | 1-25 |
| Flame spraying with powder | Flame | 3000 | Metals, ceramics, polymer materials | 30 | ◕ | 7 |
| High-velocity oxygen fuel (HVOF) spraying | | 3000 | Metals, carbides | 600–1200 | ○ | 14 |
| Symbol: ○ very high; ◔ high; ◑ average; ● low. | | | | | | |

This study contains an extensive, richly illustrated literature study, including a significant contribution of theoretical studies and practical work, as well as our own original achievements regarding the current development trends of these technologies using metal powders and ceramics. Powder production combines all the technologies discussed in this paper. In many cases, these operations are autonomous, although in many cases they are only a fragment of a complex technological process. Over the past decades, the scope of technologies using metals and their alloys powders or their mixtures with non-metallic powders, including ceramic powders, which have generally been subject to the rigours of the concept of cyber-physical Industry 4.0 systems has significantly developed. This factor determines their wide practical application, and this paper presents the scope, purpose and use areas of the technologies listed.

## 2.1. Thermal spraying

During thermal spraying [64,65, 69-76], molten or pasty coating material is applied to the surface of the previously prepared substrate (Fig. 3). The coatings use pure metals, metal alloys, ceramics (oxides, carbides, nitrides, borides and some glasses), phases and metallic compounds (sulphides, silicas, cermets, intermetallic phases), some polymeric materials (which are not in the scope of the interest of this paper). Coatings of these materials are applied to a substrate made of materials that are much less costly or more readily available than a coating, including metals, ceramics, glass, some polymeric materials, wood and paper. Most often, the thermal spray method is used to apply metals to non-metallic materials. This method was called spray metallization (SM). It also applies to the application of ceramic, composite and polymer coatings.

The powder of the covering material, solid or powder wire or rod as feed material is placed in a gas flame, electric arc or plasma, where it is melted and ground by a stream of gas such as argon, nitrogen, or compressed air or in a gas flame. The gas stream, entraining liquid particles with a diameter of 0.01-0.05 mm, directs them to the surface of the coated element, against which they hit, cool on it and join with it. Little heat is transferred to the substrate, as a result of which its temperature only rises to 100-250°C. Therefore, thermal spraying does not cause structural changes or plastic deformation of the substrate. The sprayed coating has a layered structure with different pore concentration, which can reach up to 20%. The thickness of the coatings is
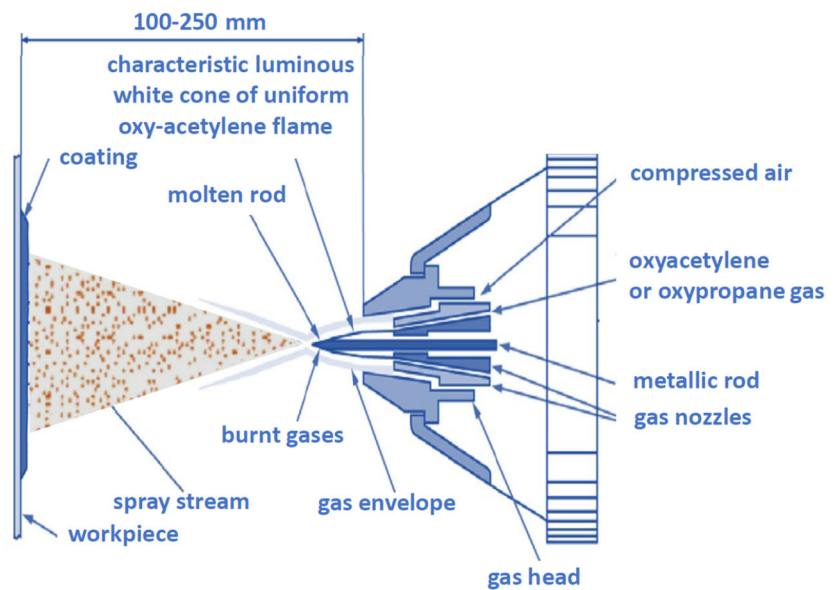


Fig. 3. Diagram of an oxygen-acetylene torch for thermal spraying

generally higher than the thickness obtained by other surface coating technologies and is usually in the range of 0.05-2.5 mm, although it can reach up to 12 mm. The obtained coatings can also be thinner than other methods [64,65,77].

These types of covers can be, among others used for thin and precise elements and for substrate materials susceptible to heat, e.g. for polymeric materials. The spraying operation can be performed both at the contractor of the structure, in the assembly hall or at the place of activity of the object. It reduces the transport and assembly costs that occur in, e.g. plumbing.

The use of thermally sprayed coatings is increasing year by year. These technologies are gaining application in various industries, mainly in the automotive, shipbuilding and aviation industries, but also in chemical and petrochemical industries, electronics, medicine, as well as in the machinery, space and defence industries. Thermal spraying methods are often used to apply metals to non-metallic materials as metallization SM.

Depending on the expected utility functions obtained by the products as a result of thermal spraying, different materials are used. Corrosion protection in urban, industrial and marine environments and increasing the durability of steel structures in such areas as bridge structures, petrochemical industry, automotive industry, shipbuilding industry, railways, electrical engineering, construction, road industry, provide zinc or aluminium coatings, successfully used since the 1930s. Thermal spray coatings can provide surface hardening, can be used to repair surface defects. Thermal spraying of Cu, Al or Ag on the surface of weak conductors or non-conductive materials, e.g. made of glass or polymeric materials, allows for electrical conductivity.

In turn, the surfaces of conductors can be coated with $Al_2O_3$ insulation layers. By spraying aluminium on the glass surface, it is possible creation mirrors that provide light reflection. Spraying coatings on medical and dental implants made of cobalt and titanium and their alloys provides increased surface porosity and ultimately facilitates the adhesion and proliferation of living cells after implantation into the human body. Precious or high-cost metal plating is used when conventional cladding cannot be done. Thermal spray coatings often provide the expected decorative effects of various products and even architectural objects.

Negative features of the thermal spraying process include losses in the material used to make the coatings. Some of the sprayed particles do not settle on the substrate material. The particles on the periphery of the spray stream are rapidly cooled, have a lower speed and, as a result, not enough energy to deform and consequently deposit on the surface of the substrate. For coating materials with a low melting point, some of the particles evaporate. The amount of these losses resulting from the essence of the technological process depends on the one hand on the melting temperature and evaporation of the coating material, and on the other hand – on the spraying method, design solution of the spray head and spraying conditions, and mainly on the spraying distance. Therefore, the amount of losses resulting from the use of different coating materials and heads of various designs can have a significant impact on the costs of coating production.

## 2.2. Flame spraying

Flame spraying [75,76,78,79] is recognized as the most popular and widespread thermal spraying technology. The coating of the sprayed surface occurs only through flue gases or additionally supplied atomizing gas, which can be air, and the sprayed particles reach a speed of 100 to 350 m/s (Fig. 4). The material intended for the coating can be fed in the form of powder or wire, and the heat source is a gas flame at a temperature of about 3000°C, most often resulting from the combustion of acetylene in oxygen.

In order to perform flame spraying, gas flame burners are used, to which the applied material can be supplied in the form of wire, rod or powder. When spraying, the powder is fed directly to the flame with compressed air or an inert gas (argon or nitrogen). Alternatively, in simple systems, the powder is drawn into the flame. The powder must be heated sufficiently during the flame flight. The powder is fed to the centre of the flame ring. Another nozzle feeds a stream of compressed air, forming a ring around the flame.
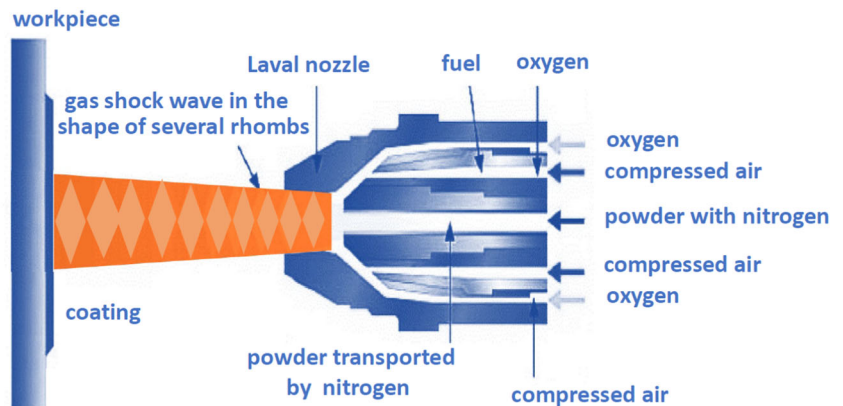


Fig. 4. Supersonic spraying diagram

Compressed air accelerates the powder particles and focuses the beam of sprayed material. When using a coating material in the form of wires, it is necessary to maintain a balance between the speed of the wire entrance into the flame and the flame characteristics to achieve continuous fusing of the wire and formation of the fine particles of the sprayed material. The compressed air ring atomizes the molten material and accelerates towards the sprayed surface.

Due to the relatively low temperature and relatively low speed of the particles of the sprayed material, the obtained coating as a result of flame spraying is characterized by porosity up to 10% and relatively small adhesion. Flame spraying is used if it is necessary to reduce costs, while lower quality coverage is acceptable. Typical applications include corrosion protection of components and entire structures, and regeneration of worn components (usually steel or copper alloys).

High-velocity oxy-fuel (HVOF) ultrasonic flame spraying [80-85] allows the coating to increase its density and improve its adhesion to the substrate. The sprayed droplets are lifted by the supersonic stream of hot gas, then hitting the substrate with high kinetic energy. During this type of spraying, the material is fed into the torch as a powder. As a result of continuous combustion inside a special chamber of a mix of gases (or oxygen with aviation gasoline), high pressure is generated, and then, thanks to the use of a special expansion nozzle, a gas stream of supersonic speed is obtained, which allows the application of particles of the selected material to the coating with significant energy kinetic (Fig. 4).

## 2.3. Arc spraying

Arc spraying [86-88] is one of the simplest thermal spraying methods using an electric arc. The role of the electrodes between which the discharge occurs is a pair of wires from an electrically conductive material, solid or powder fed at the same speed (Fig. 5). The gas stream fed

into the arc area causes the molten metal to be sprayed and directs it to the substrate. The molten material is atomized with compressed air and accelerated towards the substrate. The material particles, hitting the substrate, cool rapidly and solidify to form a coating. The wire diameter is usually 2-5 mm, and the particles can reach speeds up to 150 m/s. The burner is usually powered by 5-10 kW, the temperature in the arc can reach 6100°C at 280 A. The arc voltage is usually 20-40 V. A layer with a porosity of 10-20%, typically 0.1-1.5 mm thick is obtained.

A correctly carried out arc spraying process is called a "cold process" because the temperature remains low, which prevents damage to the substrate, its deformation and changes in chemical composition. However, this is not always desirable. The application of a hot layer to a cold substrate leads to the generation of higher stress during cooling. For this reason, sometimes an arc burner is used to heat the substrate.

Coatings made using this technique are usually denser and more reliable than those applied by flame spraying. Low costs, high application speed and efficiency mean that arc spraying can cover large areas. The disadvantage of arc spraying is the need for wires, including powdered, electrically conductive wires. If there is a need to heat the substrate during the application, a separate heat source must be used. In addition to wires from uniform metals and alloys, wires consisting of a core and a sheath are used (e.g. WC-$W_2C$ in a Co matrix), and usually, the sheath has a 50% share in the composition.

The main applications of arc spraying are:
- zinc or aluminium anti-corrosive coatings also for large components (e.g. bridges),
- regeneration of machine elements,
- abrasion resistant coatings (wires with core and sheath).

### 2.4. Plasma spraying

Plasma spraying [89,90] involves heating the applied material to plastic or liquid state and using it to the surface by a plasma stream, which is created in an electric arc, glowing between the electrode (cathode) and nozzle (anode) (Fig. 6). The plasma temperature can reach 8000-20000°C, which necessitates the intensive cooling of the nozzle. All possible materials can be used for spraying, and the quality of coatings is very high because they are characterized by minimal porosity and very good adhesion to the substrate. It is due to the very high speed of the molten particles of the sprayed material in the plasma stream. Powder of the coating material is introduced through the gas transporting it into the
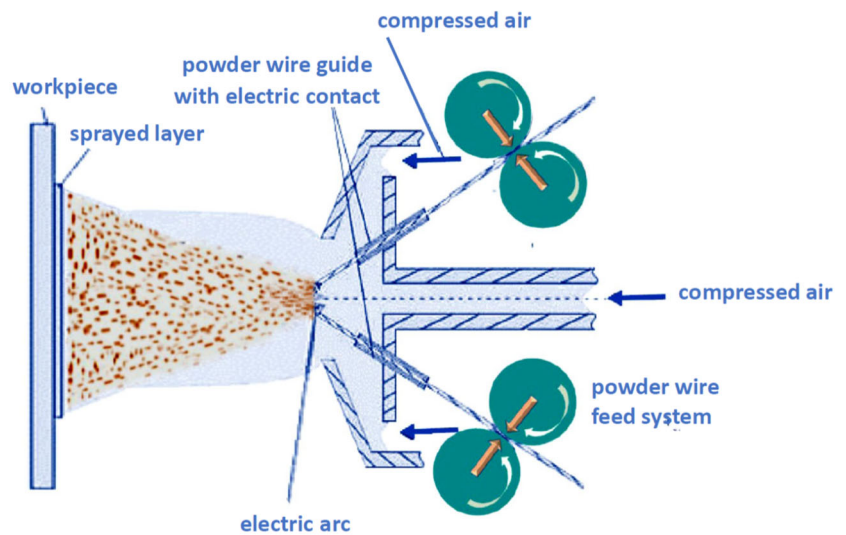


Fig. 5. Diagram of the arc spraying device

plasma stream inside or outside the plasmatron nozzle. The high speed of the plasma jet is caused by the thermal expansion of the gas flowing out of the nozzle.

### 2.5. Detonation gun spraying

The essence of the technology of detonation gun spraying (DGS) coatings on metal substrates [91-95] is the use of the explosive combustion energy of a gas mixture to heat and give the particles of powdered coating material the necessary kinetic energy. In this method (unlike the others), the most favourable conditions for forming the coating occur when the particles of the applied powder are slightly softened when they come into contact with the surface of the substrate. Lightly softened powder particles forming the coating material are by detonation applied to the surface of the substrate and in connection with it deform, causing it to crumple and thereby strengthen. As a result of the very high kinetic energy of the powder particles carried by the detonation wave, a coating with very good performance properties is formed, despite the relatively low thermal effect on the substrate.

Figure 7 schematically shows the structure of the detonation gun. Some guns allow detonating of the inner surface of pipes. Depending on the materials used, the detonation process of coating application should use strictly defined explosive mixtures, mainly acetylene and oxygen (for the implementation of refractory metal oxides, cermets and ceramic sinters) or natural gas with air (for the coating of refractory metals), but also propane-butane, methane and hydrogen with oxygen. A properly selected flow of the explosive mixture and transporting gas, as well as the spraying distance, ensure favourable spraying conditions by

providing the required level of detonation energy, which determines the quality of the coatings obtained. The constant speed of detonation also depends on the geometrical features and roughness of the internal surface of the barrel of the detonation device as well as the type, granulation and morphology of the sprayed powder coating material. Powder granulation should prevent grain overheating above the melting or evaporation points. In the case of self-disintegrating powders, the formation of detonation coatings is difficult, since such coatings exhibit unfavourable porosity. Powders with too much granulation after previous application are in turn pulled out of the substrate as a result of erosive action on the front of the two-phase metallization stream.

Regardless of the design solution of the detonation device used, the following elements of the working cycle are distinguished in the technological process of coating application:

- introducing the explosive mixture into the detonation chamber closed on one side,
- simultaneous administration of powder, coating material and neutralizing gas (usually nitrogen), preventing self-ignition,
- ignition initiation and detonation of the explosive gas mixture and creation of a shock wave spreading powder particles,
- forming behind the front of the detonation wave the metallization stream moving with the detonation wave towards the open mouth of the barrel, with increasing speed and temperature,
- forming the coating as a result of impact with high kinetic energy of a mixture of powder particles and dynamic gases on the substrate material,
- nitrogen flushing the barrel after each work cycle.

As a result of multiple repetitions of a unit work cycle with a frequency resulting from the explosive mixture and powder material used, a coating with low porosity and very good adhesion to the substrate is formed. The structure of the coating consists of successive layers with strong anisotropy, with flattened, parallel oriented grains with high cohesion and low porosity. The substrate temperature usually does not exceed 100°C, and additional cooling allows the substrate to be kept at room temperature. For this reason, the substrate may be polymeric or even textile materials. Detonation coatings on metallic materials show about 20% greater strength compared to the core, and the depth of the reinforced layer depends, among others on the type of substrate material and powder. Detonation coatings show very good wear resistance, high hardness, static and fatigue strength, corrosion resistance and good thermal insulation properties.
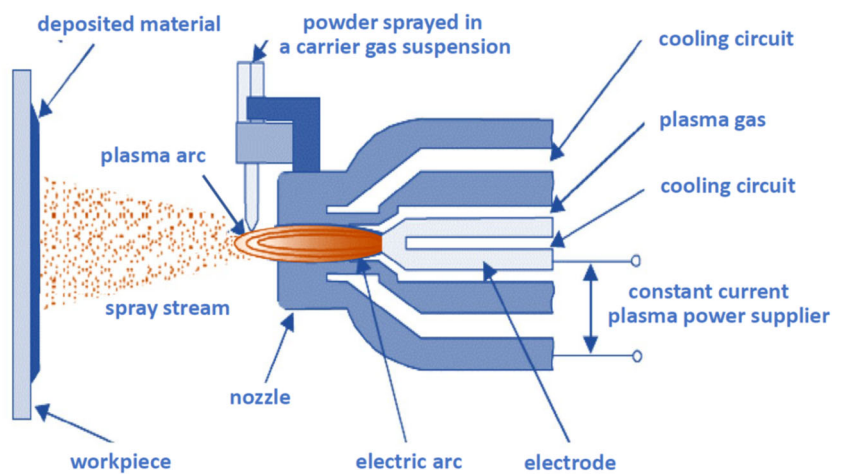


Fig. 6. Diagram of the plasma spray torch

Detonation gun spraying (DGS) is one of the possible technological variants of detonation hardening as a strengthening of metal by the shock wave arising as a result of rapid evaporation of the substrate material under the influence of external factor energy (electron stream, photon stream or explosives). Depending on the external factor used, there are the electron, laser and explosive curing. Due to the relatively lower cost of coatings production, equipment durability and low service requirements, the method of detonative coating application is competitive to the HVOF supersonic flame method.

This method is one of the technologies widely used in practice to shape the structure and surface properties of engineering materials. It is the subject of numerous studies performed in various scientific centres around the world. Detonation coatings have found wide application in heavy machinery, nuclear, textile, paper, mining, aerospace and rocket industries. It is used for the most heavily loaded aircraft parts including turbine blades and turbine compressors, seals and bearings, flap guides, wing hinges, gearing, hydraulic and fuel pump parts, leading edges and propeller blade joints, chassis components, and aluminium alloy levers and compressor blades titanium alloy. This method produces layers with an amorphous-fine-crystalline structure (amorphous matrix with fine crystalline inclusions of supersaturated solid solutions and hard-melting phases). It is also possible to provide coatings with an intermetallic phase structure using aluminium, in particular, FeAl and $Fe_3Al$ for applications in the automotive and energy industries.

## 3. Welding methods for producing thick-layer coatings on substrates made with various methods

A broad area of using powders of metals and their alloys as well as ceramic powders are welding methods for

producing thick-layer coatings on substrates made with various methods. This issue has been extensively described and documented by literature sources in very extensive own works [63-67, 96-98]. Hence this paper is limited in this part to quoting almost exclusively these works.

## 3.1. Hardfacing

In the event that the substrate metal melts during the application of the surface layer, the process is hardfacing [63-67, 96-99]. For high-quality bonding to the substrate, the applied material is given in the form of powder, as other types of source materials are not in the scope of interest of this paper. These technologies are widely used for the production of machine elements with a refined surface layer that increases resistance to corrosion, abrasive wear, erosion, cavitation, and sometimes – heat resistance and creep resistance during production surfacing.

The hardfacing processes are performed only with additional materials with chemical compositions signify-cantly different from the chemical composition of the base material. The hardfacing can be carried out, among others using powders with a grain size in the range of 40-80 μm.

The hardfacing coating material can be metals and alloys, cermets, ceramics. The most important, however, are low- and high-alloy steels, corrosion-resistant, high-carbon alloys: Fe, Ni, Co, Cu and Al, pure metals, including: Zn, Al, Ti, Ni and Zr. In order to regenerate and manufacture machine parts, manufacturing or regeneration of surface is used, respectively. One of the modern and economical solutions for the regeneration of worn machine and equipment elements and the production of new parts, especially with large working surfaces, flat or curved, and in cases where the weight of these elements is not the most important criterion, unlike wear resistance, are abrasive plates with a maximum surface of 3000×1500 mm. Abrasive pipes with diameters from 80 mm to 1000 mm are also produced. Abrasive plates and pipes are attached to the regenerated base by hardfacing, as replaceable liners for excavator buckets, internal and external pipe surfaces, chutes, cones and chutes, screw conveyors, rollers and crusher plates. Abrasive plates can be cut to any size and shaped under the different radius of curvature. You can also specify unconventional ways of using the hardfacing technology, e.g. for hardening the surface of drills used in dentistry and also for glazing the surface of paving stones.
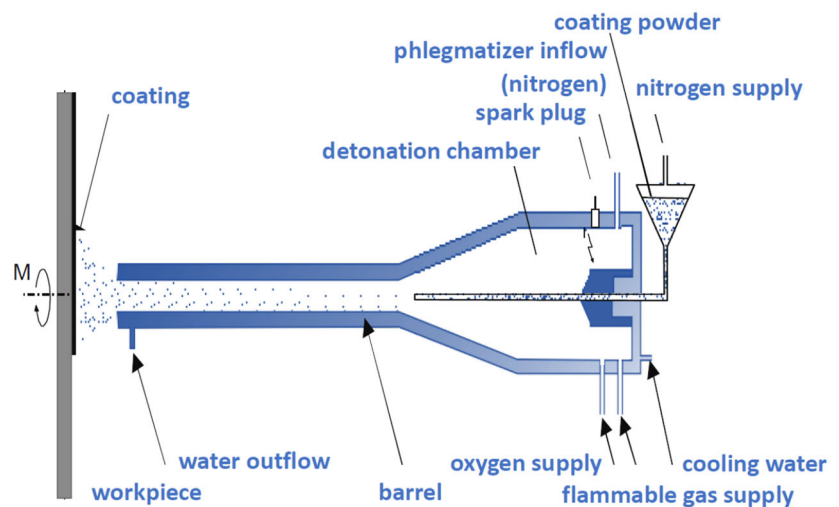


Fig. 7. Diagram of the device for the detonative application of metal powder coatings

Hardfacing process requires thorough preparation of the substrate surface, which should not show defects, especially cracks. To reduce thermal stresses and minimize deformations in the applied hardfacing, as well as to prevent the formation of brittle intermetallic phases on the hardfacing-substrate border, a preliminary weld is carried out. The thickness of the hardfacing layers in one pass, depending on the method used, is 0.05-100 mm. The choice of the hardfacing method depends on the type of treated elements, type of material, its condition and weldability, required properties, coating thickness, surface condition, variety of additional materials and process efficiency. Depending on the hardfacing technology, the share of the substrate material in the structure of the hardfacing can reach several dozen percents. Surfaces should not have defects and discontinuities, which are allowed only in the case of hardfacing with stellites. The structure of the hardfacing can be divided into the substrate material, the hardfacing and the heat-affected zone. The hardfacing has a dendritic structure, and the arrangement of the main dendrite axes reflects the direction of heat flow during its crystallization. However, the hardfacing are characterized by heterogeneous chemical composition resulting from solidification condi-tions, manifested in dendritic microsegregation, the degree of which depends on the cooling rate. Particularly strong heterogeneity occurs near the fusion line due to the lack of thorough mixing of the molten native material.

At the fusion border, the share of native material is greater than in the hardfacing, especially when there are significant differences between the chemical composition of native and additional materials. Depending on the method of hardfacing, the width of the zone adjacent to the fusion line, in which there are significant differences in chemical composition, can be 0.2-0.5 mm.

### 3.2. Laser hardfacing

Modern hardfacing technologies use the energy of the laser beam [64,97]. In general, the importance of laser machining used to shape the structure and properties of engineering materials has increased significantly over the past few decades, despite significant competition not only from other modern welding processes, but also from other methods of surface treatment of engineering materials. This is confirmed by numerous opinions of experts participating in the Delphi method foresight research. In addition to the methods of fusing ceramic powder particles, mainly carbides, with the use of laser beam smelting, which method undoubtedly belongs to the discussed group of technologies, other methods of laser surface treatment of engineering materials in which metal and ceramic powders are used are described. This mainly applies to the surface treatment of metal tool materials, although one can also imagine an analogous method of processing other materials. Laser surface treatment of materials is one of the most avant-garde and effective manufacturing engineering technologies. The interaction of the laser beam on the surface of the processed material causes the absorption of thermal energy and, as a result, melting of the surface layer and penetration into the material of the part of the absorbed thermal energy, and consequently a large temperature gradient between the molten layer of material and the non-molten substrate. A large temperature gradient influences the solidification of the melted and mixed-surface layer material and ensures appropriate properties of the obtained layer.

By adapting lasers to an increasingly wide range of industrial applications, in addition to direct lasers, beam delivery systems have been developed that enable them to operate in three dimensions for machining objects with complex spatial shapes. The wavelength of the laser radiation generated by lasers using solids as well as diode lasers allows the use of optical fibres for their transport, arranged similarly to electrical wires from the laser source to the workplace. Corrective devices are installed along the length of fibre optic cables to prevent beam degradation. The latest generations of optical fibres used in the laser industry have up to six cores – from 0.15 mm to 1.5 mm in diameter, allowing to supply several workstations at the same time, or split the power supplied to one workstation to several optical fibres.

Laser surface treatment involves the interaction of the laser beam on the surface of the workpiece and the absorption of heat energy. As a result of the melting of the surface layer and penetration into the material of the part of the absorbed heat energy appear a large temperature gradient between the molten layer of material and the unmelted substrate. During remelting, as a result of convection, the material is mixed in the molten layer. The convective movements of the material are caused by the temperature difference between the melted surface and the bottom of the melted area, and by the blowing of shielding gas and the interaction of the laser beam. A large temperature gradient causes the solidification of the melted and mixed-surface layer material. As a result, surface layers with tenths of a millimetre to several millimetres thick are obtained, ensuring the use of relatively cheap substrate material and increased operational properties of the surface of machined elements.

The basis of all laser technologies using metal and ceramic powders is the remelting of the surface layer of the workpiece called the laser remelting of the surface layer [97], which is accompanied by plasma formation and material evaporation. The plasma shields the surface before further laser heating, while actively acting on the surface of the pool of molten material by increasing pressure and mixing the molten material. In the place of penetration of the laser beam, a funnel-shaped cavity is forming in the pool, on the surface of which the hydrostatic pressure of the liquid from the side of the molten material and the vapour pressure from the bottom of the beam. The unstable balance between these interactions is disturbed continuously, among others by the relative movement of the workpiece and the laser beam. As a result, the relative motion of the cavity towards the non-melted material occurs, i.e. opposite to the movement of the element with respect to the beam. The vapour pressure fills the cavity after it moves. However, the process is accompanied by the formation of a natural outflow on the edge of remelting. Therefore, the surface of the melted material has grooves similar to those found on welding joints. Said effect can be weakened by plasma blowing by an inert gas, preferably when the reflected primary laser radiation is re-directed to the treatment zone through a flat mirror system or a mirrored bowl. Protective gas also protects the optical elements of the laser head against the formation of gases, vapours and solid particles formed during processing.

### 3.3. Laser alloying

Laser alloying [100-103] involves the simultaneous melting of alloying material, including in the form of powder, and substrate through a laser beam with intensive mixing in a liquid pool. Depending on how the stop additive is introduced into the liquid pool, remelting and feeding are selected. The alloying process consists of applying the alloying material to the substrate and then melting it together with the surface layer of the substrate material. The alloying material is applied to the substrate material, among others in the form of powders (with powdered ferrous alloys, boron carbides, tungsten, titanium), thermal spraying (plasma, flame, detonation), spraying with suspensions. By conduction of heat from the bath, a thin layer of solid material

adhering to the pool material is also melted, resulting in a very thin diffusion zone, 10 μm thick, after cooling at the interface between solid and liquid phases. In some cases, the alloying elements diffuse even to a depth of 200-300 μm. Alloying is carried out with one or more laser beam passes. The material in the alloyed layer solidifies after the end of the laser beam interaction, and the substrate material in its vicinity undergoes hardening. The structure of this layer, its chemical composition and physicochemical properties differ from the base and from the alloying material. The thickness of the layers obtained by remelting is 0.3-0.4 or 0.3-1.0 mm with impulse or continuous heating. Laser alloying may involve the introduction of non-metals, carbon, nitrogen, silicon and boron into the surface layer. Most often, laser alloying involves enriching the surface layer of materials with metals, such as Co, Cr, Sn, Mn, Nb, Ni, Mo, W, Ta, V or some of their alloys, e.g. Cr-Mo-W, Ni-Nb. Engineering steels are most frequently melted with carbon, chromium, nickel, molybdenum, powdered WC carbides, TiC or WC-Co mixtures, and tool steels with various mixtures of carbides, tungsten, tungsten carbide and titanium carbide, chromium or vanadium borides, vanadium carbides boron or mixtures thereof with chromium and mixtures of Mo-Cr-B-Si-Ni.

The concept of laser alloying has now also gained a different meaning. It is not only about feeding the powder into the laser-melted surface of a metal or alloy in a solid-state with heating to such a high temperature, that in a relatively thin layer on the surface a liquid is formed, which solidifying leads to a completely different alloy on the surface than the substrate. Such research results have been described previously, and they are the essence of the authors' own many works. In [104], a different approach was presented. The Authors [104] describe the adaption of rapid alloy development in laser powder bed fusion (LPBF) by using elemental powder blends. It enables a resource-efficient approach to the fast generation of alloys with varying chemical compositions. This approach was investigated with the new and chemically complex materials group of multi-principal element alloys (MPEAs), also known as high-entropy alloys (HEAs). In the paper [105], the issue of synthesis of new materials through the use of various powders is discussed. Powder bed fusion processes in laser-based powder bed fusion process have received significant attention in the obtaining of advanced engineering materials because of their higher cooling rate and better surface finish compared with conventional ones.
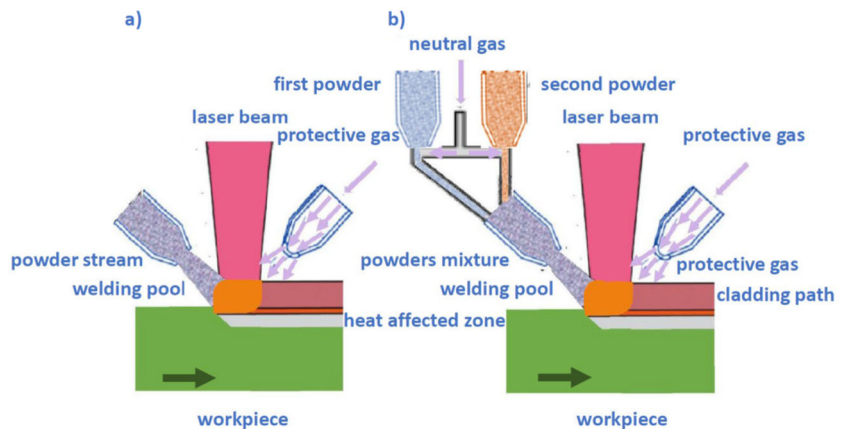


Fig. 8. Powder cladding scheme; a) powder with a powder feeder; b) two-component

## 3.4. Laser cladding

The laser cladding process [106-109] also called laser plating or laser surfacing also uses metal and ceramic powders (Fig. 8). It consists in melting a thick layer of fused material and flooding a very thin layer of the substrate material together with remelting the applied coating material, fused to obtain a coating more resistant to erosion, corrosion or abrasion than the substrate. The thickness of fused layers may be several millimetres and is higher than that of alloyed layers. Fused material may be soluble or insoluble in the substrate material. The created transition layer between the substrate and the fused layer is strongly bonded to the substrate. Melting from above is unfavourable, favouring the formation of bubbles and fusions near the substrate. Too deep melting of the substrate occurs when the laser beam energy is too high, whereas if it is too low – the melted layer has a droplet form.

In the process of injection cladding, the powder can be included by inertion or vibration, or supplied in an inert gas stream (e.g. nitrogen, helium, argon) or air. When active gas is used to provide the powder, an exothermic reaction intensifies the process. The powder or their mixture is blown into the laser beam zone, and therefore they are melted down and in this state. They fall onto the substrate, from below creating a solidifying clad layer on its surface. The laser head is coupled to a powder feed nozzle in or against the movement of the workpiece.

Laser cladding causes fragmentation of the structure and dissolution of carbide phases, resulting in a solution saturated with alloying elements after cooling. It ensures improved operational properties and increased abrasion resistance as well as improved properties at elevated tempe-ratures, although the susceptibility to cracking of molten layers increases. These properties of laser melted layers decide that they are used for corrosion-resistant materials,

tool materials, abrasion-resistant, as well as heat resistant and wear-resistant materials at high temperature. The steel is melted with aluminium, cobalt or titanium alloys, mixtures of C-Cr-Mn, C-Cr-W, Cr-B-Ni, Cr-Ni, Cr-Ni-B-Fe mixed with C and Si, Fe-Cr-Mn-C, Mo-Cr-CrC-Ni-Si, Mo-Ni, TiC-Al$_2$O$_3$-Al, TiC-Al$_2$O$_3$-B$_4$C-Al, stellites, WC carbides, TiC, B$_4$C, SiC, nitrides, including BN, chromium oxides and SiO$_2$. Nickel alloys are used for alloying, mixtures of ZrO$_2$-CaO or ZrO$_2$-Y$_2$O$_3$ with much higher mechanical and utility properties are used for alloying aluminium and copper.

## 3.5. Characteristics of the layers structure obtained by laser alloying, feeding and cladding

Laser alloying, feeding and cladding ensure the highest quality surface layers 0.1-1.5 mm thick and very high-quality substrate connections possible to use for a large part of tools manufactured with tolerances below 0.1-0.5 mm when the dimensional criterion durability does not exceed 0.5-1.0 mm [6,48,64,96,97,105, 110-148]. Hot alloy tool steels are an extensive range of such applications. Figure 9 shows schematically the mechanisms that determine the strengthening of laser processed steels. As a result of laser remelting of the tested steels, the remelting zone (RZ) and the heat-affected zone (HAZ), whose thickness depends on the laser power used for remelting, can be indicated in the surface layer. Remelting steel without introducing alloying additives in the form of carbide powders into the molten metal pool causes a slight increase in the properties of the surface layers of the tested steels compared to their analogous properties obtained as a result of conventional heat treatment, depending on the laser beam power used for remelting. During laser alloying with powders containing WC, NbC, VC, TiC or TaC, these carbides remain undissolved, forming conglomerates due to the melting of undissolved particles of carbide powder into the molten metal substrate. They may also partially dissolve in the molten metal pool, and after solidification, a composite layer with a structure radically different from the initial one is formed. The main difficulty in the laser manufacturing of composite cermet top layers with high hardness is the tendency to crack in the area of the top layers and in the heat-affected zone of the substrate, due to diametrically different properties, structure and chemical composition.
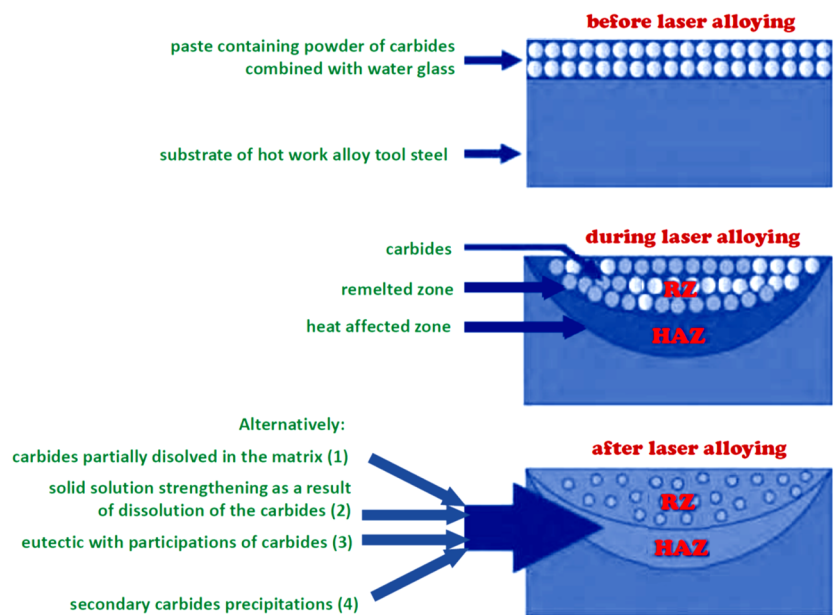


Fig. 9. Diagram of structural changes occurring in tool steels as a result of laser remelting, feeding and alloying using ceramic phase powders

The cracking tendency of the surface layers can be reduced or completely eliminated by using a gradient proportion of hard ceramic phases or a gradient concentration of the alloying component in the surface layer. It could also be made by using an intermediate layer between the surface layer and the substrate, which ensures the creation of a gradient zone and correct metallurgical connection. Gradient layers manufactured by laser technique, in addition to a very good metallurgical connection with the substrate, provide high corrosion resistance, wear resistance, high heat resistance and hardness, as well as ductility, plasticity and fatigue strength, difficult or even impossible to obtain with other technologies.

The global industry already extensively uses laser technologies. The widest industrial application in the laser processing of materials is currently solid-state lasers with an active crystalline element – Nd:YAG and gas lasers – CO$_2$. Research presently carried out in a lot of centres in the world by specialists in the field of laser technologies relates to classic technologies of laser surface treatment, alloying, feeding, cladding and laser hardfacing, including high-speed steels and engineering steels using these types of lasers. The dynamic development of laser techniques and devices has resulted in the introduction of high-power diode lasers HPDL into the world industry, which creates opportunities for further growth and a significant expansion of the use of surface treatment technology as well as alloying and laser surface treatment.

The use of the method of laser hardfacing of gradient layers is a modern approach to the problem of an additional increase in hardness and resistance to abrasive wear of new tools while reducing production costs. The technology of laser hardfacing of gradient layers with the regulation of the chemical composition during the process allows them very high accuracy in adjusting the gradient of the concentration of ceramic or metal components alloying the gradient layer. The gradient of the concentration of alloying components can be regulated at the same time by the intensity of ceramic or metal powder supply and the number and thickness of individual layer paths. The very high power density of the laser beam, reaching in the atmospheric conditions up to $10^7$ W/cm$^2$, causes that the thermal effect on the laser-treated object is very limited, resulting in minimal heat stress and small deformation. The depth of metal melting of the substrate, adjusted with high accuracy, ensures its minimal share in the surfacing. Metal layers e.g. of nanocrystalline structure, layers containing in the soft metal matrix hard intermetallic phases, cermet and ceramic layers with very high hardness, corrosion resistance, heat resistance and abrasive wear can be obtained. It is a special feature of the laser surface treatment, not found in other processes e.g. welding ones. Figure 10 shows examples of laser machined metal alloy structures.

Laser carburizing is one of the innovative methods used, among others to the surface layer of the TiAl6V4 alloy laser-alloyed using graphite powder with an average grain size of approx. 1 μm, mixed with diluted poly (vinyl alcohol) and applied to the surface of the specimen. Then the prepared layer with a thickness of about 200 μm was melted with a laser. Using different values of CW CO$_2$ laser power (1000-3000 W), as well as different Nd:YAG laser pulse frequencies (100 W), carburized layers with a thickness of 0.18-0.44 mm were obtained.

### 3.6. Electronic surface treatment using powders of metals, alloys and ceramics

Electronic surface treatment using powders of metals, alloys and ceramics includes processes and technological operations that belong to concentrated heating techniques that require melting of the surface zone and includes electron feeding, cladding and alloying [149-157].

By using rasters (grid or stripe) in the electron surface treatment process, it is possible to avoid melting too large areas connected and obtaining too large surface unevenness.
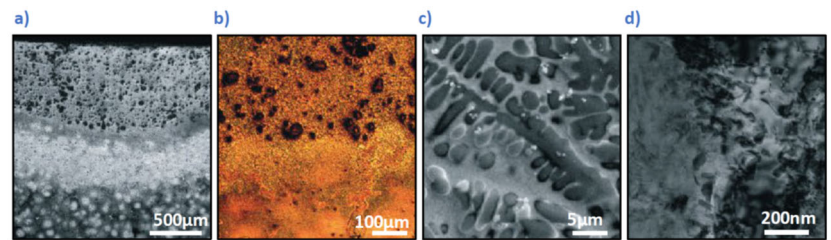


Fig. 10. Structure of laser-treated metal alloys in cross-section; a) MgAl9Zn1 alloy feeding with tungsten carbide powder (SEM); b) as in fig. a – the boundary of the remelting zone with embedded carbides and the heat-affected zone (LM); c) dendritic structure of re-crystallized eutectic carbides in X38CrMoV5-3 steel after alloying with titanium carbide (SEM): d) X40CrMoV5-1 steel after alloying with tungsten carbides (TEM thin foil)

Electron technologies require the use of electron furnaces with an electron gun consisting of two energy sources, i.e. an electron generator (emitter) (cathode) and an electron beam accelerating and forming unit. There are term emission emitters with metal or non-metal therm cathode and plasma emitters with a plasma cathode or cold metal cathode. The term emission emitters consist of a cathode, therm cathode, control electrode and anode. The source of electrons is a cathode made of a material with high emissivity and high melting point 1600-2900°C in a vacuum. Most often it is tungsten, tantalum, or non-metal tantalum hexagon. They can be annealed directly (resistance heating) – metallic or indirectly using a new therm cathode and electrons emitted from it - non-metallic. The electron beam is formed by the voltage applied between the anode and cathode from 30-100 kV. The beam's speed reaches 2/3 the speed of light. Then the beam passes through a hole in the anode and in an optical system containing one or two magnetic lenses. This beam can also be deflected, and the average power reaches up to 100 kW, with extreme values being several times larger. The density of the emitted beam is several A/cm$^2$. The power densities obtained on the charge may exceed $10^9$ kW/m$^2$. The heating time of the charge is a few microseconds, and the life of the term electrodes reaches 500 hours of work.

Plasma emission emitters operate at a lower temperature and with a smaller vacuum, are more resistant to the influence of the atmosphere, thanks to which they have a significantly extended lifetime of 5500 h. The electron emitter is a plasma glow discharge. In plasma cathode launchers, the direct emitter is a plasma glow discharge in nitrogen, argon, helium, hydrogen and methane. The electrons leave the plasma area due to thermal movements.

Further, the beam is formed similarly to thermo-emission emitters. Due to the large dispersion of the electron speed, there are defects in mapping by the focusing system, the beam current is regulated by the current and voltage of the

plasma discharge, and the method is used in technologies that do not require high precision. In the case of a cold cathode emitter, plasma with a pressure of 0.1-10 Pa is an indirect electron emitter and a source of positive ions, while secondary electron emission occurs from a cold metal cathode under the influence of its bombardment by ions and fast neutral particles resulting from collisions of ions with gas particles. Most often, the cold cathode is made of aluminium due to the high secondary emission factor. The working gas is usually air. The emission current density is the lowest and does not exceed tenths of $A/cm^2$. The cathodes with a developed surface are used to obtain the appropriate power density on the charge. The convergence angle is quite large 0.1 to 1 rad; the power of these cathodes is similar to the power of plasma cathodes; the acceleration voltage is 20-30% lower. They are used as flat cathodes for processes that do not require high precision machining.

Electromagnetic lenses are used to focus the beam and to the deflection system. The electrons emitted by the electron gun are accelerated using a voltage from 60-175 kV to a speed of about 2/3 of the speed of light and focused on the workpiece beam with a high power density. There, the electrons slow down, and the radiation energy is converted into heat. Power flux densities of more than approx. 1 $kW/mm^2$ leads to spontaneous evaporation of the material. The electron beam generators achieve power flux densities of over 100 $kW/mm^2$ and thus provide a wide area of application of electron technology. The processes of ultrafast heating and cooling are accompanied by structural phenomena entailing modification of the properties of the surface layer on an impossible scale, or at least difficult to obtain by other methods. The heating rate reaches $10^3$-$10^5$ K/s. Thus, in a very short time, it is possible to heat or melt a thin surface layer of material.

The surface electron treatment furnaces usually work in pulses, with $10^3$ to $10^5$ kW of power. We divide electron beams into continuous, impulse, and due to geometric features into linear, point, surface, and ring.

Electron heating technology can be used in the following processes using metal powders and their alloys and ceramics: alloying, fusing, remelting, glazing, as well as with evaporation, including detonation hardening. The composite layers can be created using this technology, and alloying elements introduced. After melt-free technologies, no further finishing treatment is required. After remelting, mechanical treatment is applied to give the desired smoothness. Parts with different roughness and shapes can be electronically processed. The roughness should not exceed 40 μm and the surface should be as perpendicular to the electron beam as possible. Particularly noteworthy is the

need to demagnetize the elements before electronic processing. Usually, electronically processed are large rolling bearing raceways, piston rings, ball joints, gears and crankshafts, cams, turbine blades and others.

The electronic feeding of particles of hard materials, most often carbides and oxides, serves to increase the abrasion resistance by electron remelting the surface zone and introducing these particles into it. Composite layers on the surface, with a moderate value of the introduced energy, contain preserved hard particles in the remelting zone in the matrix of the substrate, which can be dispersed if more energy is introduced. At a sufficiently high temperature, higher than the melting point of the material of these particles, they undergo dispersion or dissolution in the liquid solution of the melted material, after solidification, forming a layer on the surface in the event of dissolution with a chemical and phase composition different from both the substrate and the fed particles. The process is called electron feeding/alloying, respectively. In this way, it is possible to change the surface properties deliberately. It is one of the electronic technologies of concentrated heating. Coatings produced by electronic processing show properties not available by classical methods.

### 3.7. The use of metal powders for the manufacturing of powder wires used in the application of surface layers by welding methods

A broad area of application of metal powders that are the main focus of this paper is welding technologies used for coating applications [158-160]. These powders can be used directly in these technologies, as well as have found application in the production of some welding consumables. They can be powdered wires also called cored wires often filled with powdered metals inside, among others nickel and chromium, in addition to flux (outer shield) or chemicals that produce protective gases (inner shield) during welding. The production of powder wire is carried out from a steel strip formed as a U-shaped boat with the use of shaped rollers, into which a powder mixture with metal powders is poured. Then the wire is formed by forming in subsequent rolls, and its cross-section becomes closed and circular, and when pulled through the diamond mesh, its diameter is reduced, usually to 0.9 or 1.1 mm. Powders are used to manufacture some coated electrodes for welding, consisting of two components: the coating and the core. The metallic part of the electrode can be in the form of a powder wire, and then fluxes are not placed inside the wire, or their proportion is smaller. The electrode cover consists of mineral raw

materials, ferroalloys, metals and organic components in a ratio appropriate for the given electrode grade. The most commonly used mineral raw materials for the manufacturing of lagging are iron, manganese, titanium, aluminosilicates (e.g. kaolin, field splinter, feldspar), calcium, magnesium, iron, fluorine compounds (most often fluorite) and silica (quartzite). Organic components such as cellulose, wood flour, starch, dextrin are introduced into lagging in relatively small proportions, mainly to produce gases that shield the welding pool from the atmosphere of air. Due to the use of additional materials containing metal powders, some technologies using these materials have also been analysed in this paper as subsequent applications of metal powders in the technique. These technologies also include the specific applications of conventional hardfacing methods.

Binder, among others in the form of metallic powder or powder wire, can be used for arc welding. Manual arc welding with a coated electrode consists in melting the electrode material and metal covered with the heat of the electric arc. For applying coatings as additional material, among others, coated electrodes with powder core containing metal powders rutile basic.

A thick layer can be laid in one pass 1-5 mm. Due to high versatility and low costs, the method is widely used for laying welds from low-carbon, low-alloy, high-alloy, special steels, cast iron, Ni, Cu, Al, Co alloys, and welded objects can have any shape at an arc temperature of up to 5000°C, the substrate it undergoes significant melting, so that its share in the brew reaches up to 40%.

Arc welding with a gas metal arc welding (GMAW), metal inert gas cladding (MIGC) and metal active gas cladding (MAGC) consists in fusing the electrode material and the substrate by a glowing arc between the consumable electrode and the welded surface in an inert or active gas shield. As additional material used, include powder wires. Shielding gases are argon, helium and $CO_2$, and the type of gas shielding depends, among others chemical composition and properties of the deposit. The technology is used for surfacing large, flat surfaces with layers of special performance properties, or for regenerating low carbon and low alloy steel, cast steel, cast iron, Cu and Al alloys.

Arc hardfacing with a gas tungsten arc welding cladding (GTAWC) or tungsten inert gas cladding (TIGC) involves
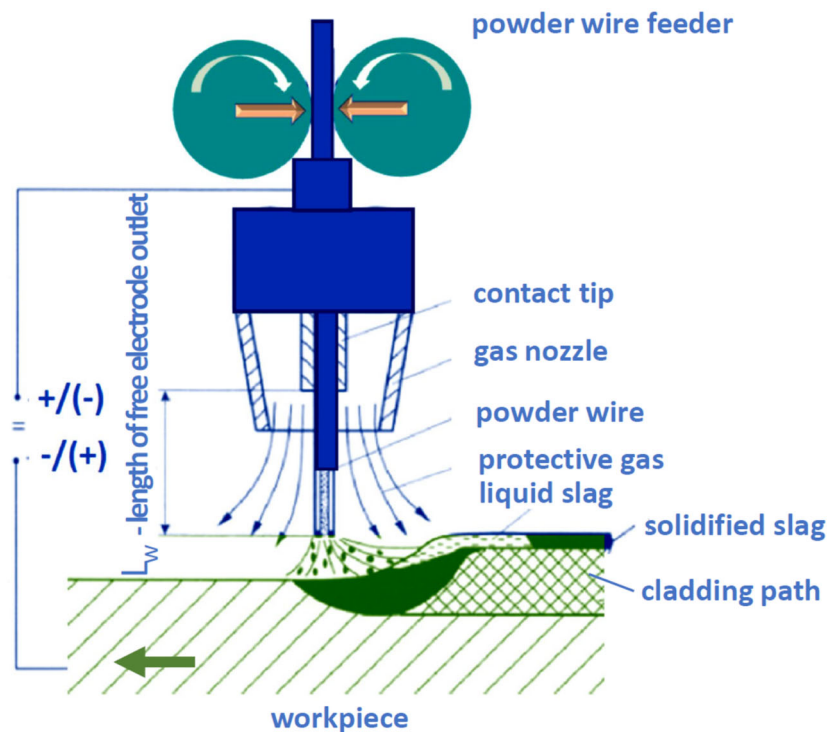


Fig. 11. Diagram of arc welding with powder wire in a gas shield

the introduction of additional material into the arc area glowing between the non-melting tungsten electrode and the hardfaced workpiece in inert gas shield (Fig. 11). Additional material, among others in the form of a powder or powder wire it melts and forms a hardface on the molten surface of the object. Low performance and hence high cost, with high quality, is the reason for using this technology for hardfacing, primarily repairing machine elements and repairing casting defects. The share of the substrate material in the hardfacing reaches 5-10%, and the thickness of the layer in one pass is 1.5-5 mm, and the use of an inert gas shield (argon, helium) ensures its high quality. The technology is used for steel, cast iron, aluminium alloys, copper, and as coatings: stellites, high-alloy steels, including austenitic, lead, copper and nickel alloys.

Plasma hardfacing involves melting in a plasma arc with a temperature of 18000-24000°C of additional material, among others in the form of powder with grains of 0.06-0.3 mm with the slightly melted ground. The powder is introduced into the plasma torch from the dispenser by means of a transporting gas, usually argon, providing accurate protection against air access so that after melting in the plasma arc coming out of the nozzle, it is transferred by gases under pressure to the substrate, creating a deposit with a minimum proportion of substrate material and thickness 0.25-6 mm in one pass. The additional material is

a powder-based on cobalt, nickel, iron, chromium, copper and tin. Plasma surfacing is used for parts of internal combustion engines, cutting tools, cutting edges of earthmoving tools, valves, valve seats, metallurgical roll plugs, drill string joints made of non-alloy steel, corrosion-resistant steel, cast steel and some types of cast iron. When the wire is used as input material, it is sprayed. Plasma welding with preheated wire before entering the plasma arc area is an entirely automated process, ensuring less melting of the substrate and greater welding efficiency than when using cold wire.

Binder, among others in the form of metallic powder or powder wire, it is often used for gas welding. It involves applying a layer of liquid metal melted in a gas flame to the molten surface of the object. The primary flammable gas used in gas welding is acetylene with a flame temperature of approx. 3100°C. Oxygen acetylene welding requires exact flame regulation, for most alloys a slightly carburizing or neutral flame is recommended, only for copper alloys – a slightly oxidizing flame. Very often, preheating and slow cooling after surfacing is necessary. Fluxing is recommended for some alloys.

The method of gas hardfacing is applied for achieving the smooth, even coatings of high quality, with minimal melting of the substrate material, whose participation in the hardfacing is very low compared to other hardfacing methods. High-alloy steels with a high proportion of carbides, nickel alloys and cobalt are applied by this method. In practice, gas hardfacing of machine parts and devices is most often used with heat-resistant Co-Cr-W alloys with 1-3% carbon – stellites and similar very hard materials, resistant to abrasive, adhesive, corrosion and erosion. The binder can be fed through a hopper or a powder feeder. One example is the use of a binder placed in a metal tube with the addition of diamond powder (Fig. 12). This method has been patented in the USA, and the application of the padding can be carried out by gas or arc method.

## 4. General characteristics of special technologies for manufacturing gradient materials using powders of metals, their alloys and ceramic materials

Special technologies for producing thick-layer covers using metal powders, their alloys and ceramic materials on substrates made by other methods, in fact being hybrid
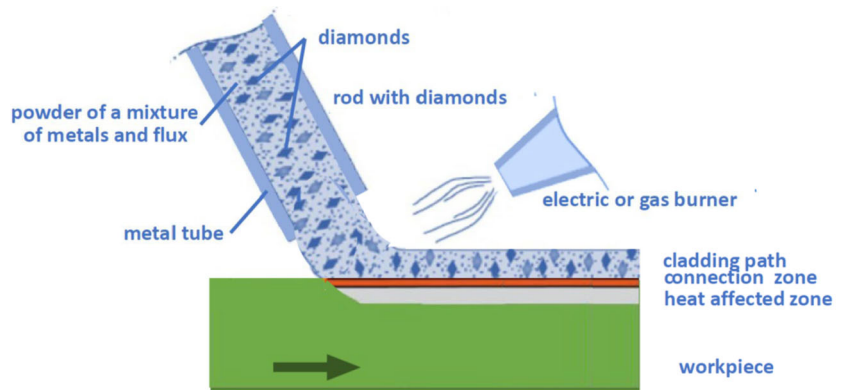


Fig. 12. Method of applying a diamond powder reinforced surfacing

technologies, is the production of gradient materials using powder metallurgy. These technologies enable the production of tool gradient material TGM, which can also be used with ceramic powders. Modification of the classic powder pressing in the matrix allows for the creation of tool material with a continuous or discrete gradient structure in its entire volume.

This highly specialized powder metallurgy technology [62,64,161-174], for example, is applied for a gradient tool material manufacturing by sintering a non-alloy steel powder or possibly a mixture of iron and graphite powders with a chemical composition corresponding to non-alloy steel, surface-enriched with high-speed steel powder, with the proportion increasing as it approaches the surface. The top layer, resistant to abrasive wear, is then high-speed steel and the core is unalloyed steel. The purpose of manufacturing a gradient material with such a selected chemical composition and structure is to reduce the consumption of high-speed steel and increase the ductility of the core of such tool material. High-speed steel manufactured with this specialized powder metallurgy technology and surface-reinforced with hard carbide, nitride and/or oxide phases, e.g. NbC, VC, WC, TiC, TiN, VN, BN, $Al_2O_3$ and $ZrO_2$, with a thickness of 0.1-1 mm, exhibits much higher properties. It is an example of iron-based gradient tool materials. High-speed steels with a traditional chemical composition are surface strengthened, obtaining increased mechanical properties and increased resistance to abrasive and erosive wear, including at elevated operating temperatures, compared to conventional and sintered high-speed steels. At the same time, relatively high ductility of the core, characteristic for steel, is ensured. The structure of the material thus manufactured is characterized by a linear gradient of chemical and phase composition, passing from the structure characteristic of typical high-speed steel in the core of the newly formed material to the structure of higher-alloyed high-speed steels or carbide-steels constituting the surface layer.

Different techniques for forming powder mixtures are used to obtain a gradient of structure and properties of the materials manufactured. They include compression in a single-sided uniaxial die, cold isostatic pressing, low-pressure polymer-powder compacting, vibration moulding and compacting in a closed matrix, and sedimentation moulding. The most preferred method is classical compression in a closed matrix by sequential filling of matrices with powder mixtures, with the share of hard ceramic phases growing towards the surface layer, which is the working surface of the tool.

The most advantageous method of powder metallurgy for obtaining abrasion and wear-resistant surface layers of tool materials constituting the working surface of a structure gradient tool is the method of classical compression in a closed matrix by sequential backfilling of matrices with powder mixtures, with the proportion of hard ceramic phases decreasing towards the core. The use of the powder metallurgy method creates the possibility of providing the top layer with high wear resistance, which is characterized by cemented carbides and cermets while maintaining a relatively high core ductility typical for high-speed steels and traditional carbide-steels, while at the same time promoting a relative cost reduction. This material structure allows free shaping of the properties depending on the working conditions of the tool.

There is a hard layer of material in areas of the tool exposed to abrasion. In other places exposed to impacts, the structure of the tool material ensures high toughness. The newly developed appropriate technology consists in backfilling successive layers of powder mixtures with different chemical and/or phase composition (Fig. 13), depending on the required properties of the produced material, and then pressing and sintering them. Therefore, it is possible to control the output component of the compact in order to obtain a sinter with a variable chemical and/or phase composition that varies in the volume of the material along with the position on the cross-section of the product thus manufactured. The tests were also carried out to the steel substrate HS6-5-2 and HS12-1-5-5 obtained from powders and gradient layers from powders WC, TiC and a mixture of powders WC + TiC + TaC + NbC, respectively, and in some cases, the share of carbides in the outer layers reached over 30%. Exemplary structures of tested gradient materials are shown in Figure 14.

The technique of low-pressure forming (LPF) or pressure less forming (PLF) and sintering of powders can be used to produce wear-resistant coatings on steels, especially low-
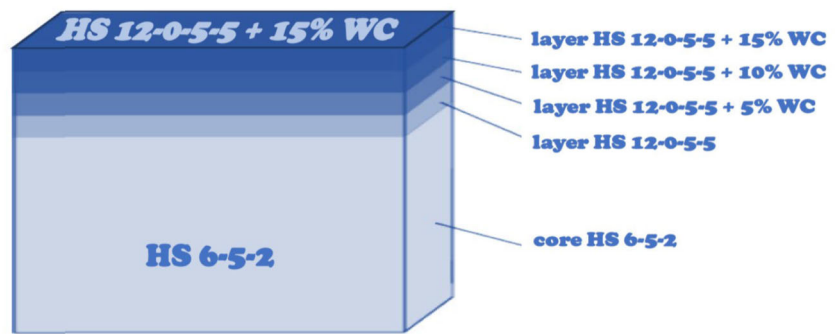


Fig. 13. An example of applying subsequent coatings to obtain a gradient layer

and non-alloy steels. This way is maintaining a relatively ductile core and abrasion-resistant surface with a carbide structure. Immediately after powder formation, a coating in the form of a polymer-powder slurry forms on the surface of the substrate, the binder of which polymerizes, cools or evaporates the solvent from it. After the forming operation, a material is obtained with a clear separation boundary between the substrate and the coating, which is a binder-powder mixture. After sintering, the clear boundary between the coating and the substrate disappears as a result of increased diffusion. Hence, the coating area can be treated as the top layer. The gradient or homogeneous nature of the surface layer structure is determined by the method of applying the polymer-powder coating on previously prepared steel surfaces. A new generation of abrasive and diffusion-resistant tool materials with a gradient of properties and structures manufactured by hybrid methods by injection or low-pressure powder moulding and sintering was also developed using this technology. A process of low-pressure forming and sintering of coatings on ready tools was also developed. The different types of binder used to fulfil the basic task and the coatings in the sintered state cover the substrate material. Cracks and delamination occur most often in coatings in which thermosetting resin is used. This is due to the rate of thermal degradation of the thermosetting resin, which affects defects in the surface layer. Similarly to high-pressure low-pressure and sintered high-speed steels, the thermal degradation process of thermosetting resin is quite difficult and requires slow heating at a rate of 0.3°C/min and a long heating time at high temperature of thermal degradation of about 500°C. The application of coatings using paraffin, polypropylene paraffin or thermosetting resin is technologically more complicated compared to coatings using varnish or water glass. This is due to the fact that the use of a thermosetting resin requires further heating at a temperature of about 115°C to polymerize the binder. The use of thermosetting resin as a binder increases the carbon concentration by about 0.5% compared to the carbon concentration in the batch

powder mixture. The degradation of the binder means that the so-called residual carbon is existing. Its concentration depends on the type of binder. This carbon, remaining on the surface of the high-speed steel powder, initiates the sintering process at high temperature. It diffuses into the surface layers of the powder grain and lowers the solidus temperature, which starts the sintering process. The binder in the form of varnish and resin causes the evaporation of the solvent in the varnish and opens the pores that allow the degradation of the varnish and resin quickly. This solution causes that the increase of the carbon concentration in the sintered coating increases only by 0.3% in relation to the carbon concentration in the feed powder.

Due to technological difficulties associated with low-pressure forming with the use of thermosetting resin and the need for very slow thermal degradation by the uncontrolled increase in carbon concentration in the surface layers after sintering, the use of a binder in the form of resin is not preferred. Using paraffin (PW), the polymer powder mixture should be heated to apply to the surface of the substrate material and the substrate material above the softening temperature of paraffin, i.e. 57°C. The adhesion of the coating in which paraffin is used is extremely good, however, it depends on the conditions of thermal degradation. Too long degradation causes detachment of the coating. The best effects are given by rapid thermal degradation carried out directly during heating to sintering temperature. An example is the extended surface of a commercial C70U non-alloy steel drill coated with high-speed HS12-0-5-5 steel powder and carbides mixed with paraffin. For both 41Cr4 steels coated with high-speed steel HS6-5-2 powder and HS6-5-2 steel powder coated with HS12-0-5-5 steel, no decohesion was found. The coating structure is characterized by the even distribution of carbides in the matrix of the solid iron solution. The substrate structure is characteristic of conventional high-speed steel and shows band segregation of primary carbides.

The technique of applying a polymer-powder coating using a binder in the form of paraffin and polypropylene resembles powder coating of metal elements. The substrate material should be heated to a temperature of about 200°C, then apply a mixture of powders with a solid binder. The substrate temperature is higher than the softening point of the binder in the fluidized bed, which causes the polymer-powder mixture to soften and cover the surface of the substrate forming a compact and tight coating. Only the surface of the coating has a high roughness, which is associated with a low proportion of binder in relation to the
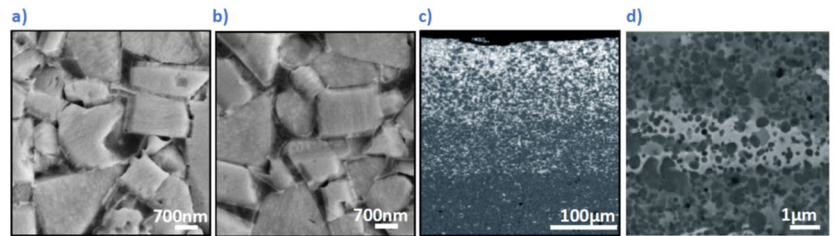


Fig. 14. Tool gradient materials structure a) a surface layer containing 9% tungsten carbide mixed with high-speed steel HS6-5-2; b) as fig. a near the core with a 3% tungsten carbide content; c) as fig. a with a 10% tungsten carbide content decreasing to 0 towards the core; d) with 25% tungsten carbide (SEM)

powder, of only 30%. The increase in the binder content reduces the surface roughness due to the increase of the liquid phase at the coating application temperature. The use of water glass as a binder causes it to appear in the coating after sintering. During heating to the sintering temperature and heating at this temperature in the $N_2$-10% $H_2$ atmosphere, water glass does not degrade, which prevents its use as a binder for the manufacturing of coatings by low-pressure moulding.

In the case of the varnish used as a binder, numerous pores can be observed in the structure of the coating, the proportion of which also depends on the sintering temperature and the time of binder degradation. Despite numerous pores, no decohesion was found between the substrate and the coatings in which the varnish was used. Higher porosity when using varnish compared to the use of, e.g. paraffin is associated with evaporation of the solvent, which initially opens the pores even before thermal degradation. In this way, the structure is similar to that obtained after solvent degradation. Hence further thermal degradation occurs quickly during heating to sintering temperature. The interlayer in the form of a powder of corrosion-resistant steel X2CrNiMoN17-11-2 can also be used. Due to the high concentration of chromium in X2CrNiMoN17-11-2 steel and high wettability of chrome during sintering, this element increases the adhesion of the coating to the substrate. The described technology is experimental and should be expected to be widespread and developed in the near future.

## 5. Summary

This paper contains an extensive, richly illustrated literature study, including a significant contribution of theoretical studies and practical work, as well as our own original achievements regarding the current development trends of these technologies using metal powders and

ceramics. The importance of technologies using powders of metal, their alloys and ceramics can be appreciated by analysing the development tendencies. In the group of technologies for applying surface layers using metal powders, metal alloys and ceramics, specific roles pay the electron beam powder deposition, detonation gun spraying and laser alloying/feeding. These methods are becoming more and more popular. It should also be emphasized that powder materials engineering, including the technologies described in this paper, are a crucial technological area on the technology platform of the generalised holistic augmented Industry 4.0 model. It makes this area of engineering particularly attractive in light of the forecasted development and, above all, the prevalence of this approach. The development of manufacturing in the Industry 4.0 phase is dependent also on the development of powder engineering.

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