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# INFLUENCE OF THE CARBIDE TYPE ON TRIBOLOGICAL PROPERTIES OF THE HARD FACED LAYERS

Branislav Nedeljković[1], Vukić Lazić[2*], Srbislav Aleksandrović[2], Božidar Krstić[2], Milan Mutavdžić[3], Dragan Milosavljević[2], Milosav Đorđević[4]

[1]*Central laboratory, Zastava cars, Trg topolivaca 4, Kragujevac*
[2]*Faculty of Mechanical Engineering in Kragujevc, Sestre Janjić 6, Kragujevac*
[3]*Company for Road Construction "Kragujevac", Tanaska Rajića 16, Kragujevac*
[4]*High technical school in Kragujevac, Kosovska 8, Kragujevac*

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## Abstract

This paper gives a theoretical review of carbide-forming – alphagenic elements and states the conditions which elements should fulfill in order to be considered carbide-forming. It primarily involves alloying elements which in the iron-carbon system can form simple, complex or special carbides, i.e. phases of interstitial and substitutional type. It also gives a review of carbide types formed during hard facing of steel parts with different types of filler materials. The paper points outs tribological properties of certain types of carbides and the effect of metal matrix in which carbides are embedded. Investigations on models suggest that, besides the applied technology, the type of filler material is of decisive importance for output properties of the hard-faced layer. The most suitable filler material, i.e. hard facing technology, has been chosen, depending on the working conditions and the type of electrodes. The results of this paper point out the importance of the right choice of filler material and welding technology which mostly affect the type of microstructure and the type of carbides.

*Key words: carbides, welding, abrasive wear, hardness, microstructure, filler material*

## Introduction

This paper gives a brief account of carbide forming elements. A special attention is paid to carbides that are formed during hard facing of steel parts with different types of filler material. It gives tribological characteristics of certain types of carbides, as well as the effect of metal matrix in which carbides are embedded. Contradictory opinions on the most suitable matrix in relation to tribological aspects can be found in the literature. Therefore, numerous experimental hard facing procedures with different filler materials

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[*] Corresponding author: Vukić Lazić, vlazic@kg.ac.rs

have been performed and properties relevant to resistance to wear have been studied. They include not only the value of total hardness but also its distribution in the cross-section as well as microstructures of hard faced zones.

## Carbides in metal base and their importance

The greatest number of alloying elements in steel and cast iron chemically react with carbon forming interstitial phases or complex structures usually called *carbides.*

Experiments have shown that the tendency towards carbide forming in steels is related to electron configuration of alloying elements. Those elements whose sub layer *d* is less occupied by electrons than in iron form special carbides. The smaller the electron number in the sub layer *d*, the higher is the tendency towards forming special carbides and, hence, the more stable carbide. Table 1 gives atomic numbers, energy state, atomic radii of important carbide forming elements, as well as ratios of carbon atomic radius and the atom radius of the corresponding element [1-9].

*Table 1 Carbide forming elements, atomic numbers, energy state, atomic radius in nm and ratio of carbon atomic radius (0.077 nm) to those radii*

| | | | | | | |
|---|---|---|---|---|---|---|
| Shell – Principal quantum number | N (4) | Ti 22 | V 23 | Cr 24 | Mn 25 | Fe 26 |
| | | $3d^24s^2$ | $3d^34s^2$ | $3d^54s^1$ | $3d^54s^2$ | $3d^64s^2$ |
| | | 0.147/0.524 | 0.132/0.583 | 0.125/0.616 | 0.112/0.688 | 0.124/0.621 |
| | O (5) | Zr 40 | Nb 41 | Mo 42 | | |
| | | $4d^25s^2$ | $4d^45s^1$ | $4d^55s^1$ | | |
| | | 0.158/0.487 | 0.143/0.539 | 0.136/0.566 | | |
| | P (6) | Hf 72 | Ta 73 | W 74 | | |
| | | $5d^26s^2$ | $5d^36s^2$ | $5d^46s^2$ | | |
| | | 0.157/0.490 | 0.143/0.538 | 0.137/0.562 | | |

In accordance with the given rule, carbide forming order goes in the direction from iron towards manganese, chromium, vanadium to titanium:

$$Ti \leftarrow V \leftarrow Cr \leftarrow Mn \leftarrow Fe ,$$

from molybdenum, through niobium to zirconium:

$$Zr \leftarrow Nb \leftarrow Mo ,$$

from wolfram through tantalum to hafnium:

$$Hf \leftarrow Ta \leftarrow W .$$

Alloying elements whose sub layer d is more occupied by electrons than iron do not form carbides in alloy steels, this is especially the case with elements with completely occupied sub layer d, like copper or zinc.

In the case when there are several carbide forming elements in an alloy steel, carbon will always bind to an element of greater carbide forming tendency. This means that in steel alloyed with Cr and V, more V and less Cr-based carbides should be expected, while for higher contents of V and Cr there are no iron-based carbides.

The carbon atomic radius is 0.071 nm, while atomic radii of all carbide forming elements are higher than 0.1 nm. When the ratio of the carbon atomic radius and the atomic radius of a carbide forming element is less than 0.59 (Zr, Hf, Ti etc.) intermetallic phases with the following characteristics are formed:

- have (or have retained) stoichiometric ratio MC or $M_2C$ (where M- metal, and C- carbon),
- have a simple crystal lattice formed by metal atoms as well as mixed lattice, usually face-centered cubic (carbides of MC type) or close-packed hexagonal crystal lattice (carbides of MC or $M_2C$ type),
- can form a crystal lattice with no carbon atoms, i.e. they can crystallize with incomplete occupancy of sites,
- are very stable compounds with extremely high melting temperatures (2000-3500°C) and almost insoluble in austenite,
- possess high hardness.

When the ratio of the carbon atomic radius and the atomic radius of carbide forming element is higher than 0.59 (e.g. Mn), carbides have a *complex structure*. Most of known carbides crystallize into three crystallographic systems: *cubic*, *hexagonal* and *rhombic*. Some elements can form two types of carbides, whereas manganese and chromium can form even three types of carbides with different crystal lattices.

The simplest carbides crystallize in a cubic system of a primitive lattice of MC type. These carbides are formed by V, Ti, Nb, Ta and Hf. More complex carbides crystallize in a hexagonal system with lattices of MC and $M_2C$ type. Only molybdenum and wolfram have hexagonal lattices of MC type, while V, Nb and Ta have $M_2C$ type lattice. The ε carbide found in hardened and low tempered steels also has a hexagonal lattice of MC type. Rhombic lattices are formed by Cr, Mn, Fe, Co, Ni carbides.

From the aspect of resistance to wear and high temperatures, it should be pointed out that chromium and manganese carbides crystallize in a regular[†], hexagonal ($Cr_7C_3$ and $Mn_7C_3$), as well as in rhombic ($Cr_3C_2$ and $Mn_3C$) system. Except for chromium carbide $Cr_3C_2$, all others are found in iron alloys, where a certain number of iron atoms can be replaced with another metal (alloyed cementite).

Figure 1 illustrates areas of existence of different phases in alloys of Fe-C-Cr type depending on the content of Cr and C. When the content of chromium is low special carbides are not formed because chromium dissolves in ferrite and cementite, giving the mixture ($\alpha$ + $(Fe,Cr)_3C$) in the field I. There is alloyed carbide $(Cr,Fe)_7C_3$ in the field II. No alloyed cementite (besides ferrite) can be found in the field III except chromium carbide with dissolved iron $(Cr,Fe)_7C_3$. Ferrite and two types of chromium carbide with dissolved iron (the first carbide $(Cr,Fe)_7C_3$ and the second carbide $(Cr,Fe)_{23}C_6$) may be seen in the field IV. There is only ferrite and the second chromium carbide with dissolved iron $(Cr,Fe)_{23}C_6$ in the field V, whereas in the field VI besides ferrite and the second chromium carbide with dissolved iron $(Cr,Fe)_{23}C_6$, an intermetallic phase of iron with chromium FeCr can also be found.

In the field VII, only ferrite and intermetallic phase of iron with chromium FeCr are found, and finally, in the field VIII only ferrite can be found. Other systems of the

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[†] Regular lattice refers to a cubic lattice.

Fe-M-C type are similar to the system Fe-Cr-C, but due to a smaller number of phases, they are simpler.

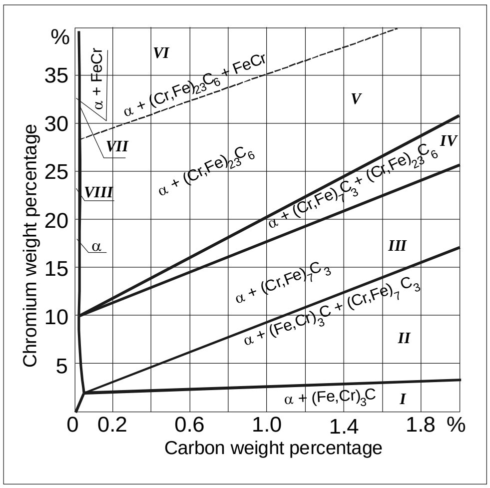


*Figure 1 Areas of different phases of Fe-C-Cr alloys at the temperature of 20ºC [8]*

When there several carbide forming elements are present in steel-filler material, carbides of elements with greatest affinity towards carbon will be first formed. For example**,** in steel with a certain content of carbon W and Mo carbides and $Fe_3(W,Mo)_3C$ are formed first, then chromium carbide $Cr_{23}C_6$, and finally the second chromium carbide $Cr_7C_3$ is formed. If there is enough carbon left cementite can be formed too.

Therefore, if the chemical composition of the filler and the main material (steel) is known**,** it is possible to predict approximately what kind of carbide will be formed. Furthermore, based on the stability of certain carbides, their solubility in austenite, i.e. thermal stability can also be predicted.

Since special carbides are less soluble in austenite than in cementite (lower diffusion rate), alloy steels should be longer kept at austenitization temperature**.** It is sometimes desirable to keep some undissolved carbides in the structure because they prevent growth of austenite grain (e.g. in fast-cut steels). Special carbides have higher hardness than cementite and martensite. When they are formed in a hard martensitic matrix, steel resistance to wear is increased; i.e. harder carbides provide greater resistance to wear. Resistance to wear is not only determined by carbide hardness, but also by its size, distribution and shape. Large and irregularly-shaped carbides may be easily pulled out of the metal matrix, especially if they are located on the cutting edge of the tool. Carbides precipitated at the grain boundaries and arranged in a line significantly decrease resistance to wear.

In some steels, time of holding at tempering temperatures influences the type of precipitated carbides. At tempering, stable equilibrium carbide is not directly precipitated; transitional carbide is initially precipitated and then it slowly transforms into an equilibrium carbide.

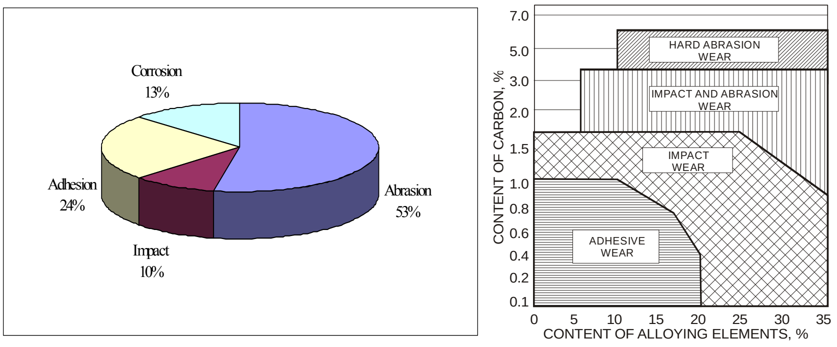
Some elements (except for Ni, Co, Fe, Mn and Cr, and in certain cases W and Mo) form interstitial phases. A representative of this phase is vanadium carbide.

Elementary lattice of vanadium carbide VC does not have to be fully occupied by carbon atoms; there can be vacancies in some vanadium lattices.

From the aspect of great resistance to wear, *wolfram carbide* is of an enormous importance. For hard facing, it is delivered in the form of full cross-section wires or steel pipes filled with carbides. Hardness of this carbide ranges from 2400-2700 HV (95 HRA), while hardness of the metal base of the hard faced metal is 45-65 HRC, suggesting an extremely high resistance to pressure, but low ductility. WC oxidizes at the temperature above 538ºC [6, 10] (so-called yellow oxide), therefore these hard faced layers are not recommended for work in corrosive environments. Hard faced metal is very sensitive to transversal cracks.

Manganese is a weak carbide forming element. It does not react with iron in steel to form separate carbide, it partially dissolves in cementite, where it replaces a part of iron atom $(Fe,Mn)_3C$.

Filler material for hard facing is mostly chosen on the base of both required properties of hard facing layer and available equipments. Wear mechanism and analysis of wear process of each particular element lead to conclusion that damages are mostly caused by friction, although sometimes it may be caused by corrosion, thermal and thermo mechanical fatigue etc. [12, 13]. If material is subjected to increased corrosion, filler material should be chosen exclusively on the base of chemical structure which may provide corrosion resistance, whereas for parts exposed to friction force choice of filler material become more complex. Nevertheless hardness and chemical structure should not be only criteria for estimation of suitability of facing material. Papers [6, 14] display short list of the most often applied filler materials specially those resistant to wear, electrochemical corrosion and oxidation. Wear and corrosion resistant filler materials for hard facing may be classified in six groups: steel, cast iron (white), wolfram carbides, cobalt alloys, nickel alloys and cooper alloys. Since the greatest number of industrial parts is withdrawn from exploitation due to wear (53% abrasive, 24% adhesive, 10% impact and other kinds of wear) and corrosion (13%) (Fig. 2a), filler materials are classified on the base of these criteria [6, 11]. For that reason, diagrams showing contents of carbon and alloying elements in alloys for hard facing for most common types of wear are given in Figure 2b [11].



*a) Different kinds of wear* *b) Alloys for hard facing*

*Figure 2 Choice of microstructures for different kinds of wear [11]*

## Experimental examination

*Models examination*

Above described tribological consideration and listing of the most important filler materials for hard facing are used as a basis for experimental hard faced models. The results will lead to a decision which of applied techniques is mostly appropriate to be used for real parts which are in service. Hard faced models with one or more passes (layers) with or without preheating were studied (Fig. 3a-c). Metallographic samples-blocks were cut from hard faced models as shown in Figure 3d. Hardness was measured in different directions of the block in order to estimate microstructural characteristics of surface zones. Samples are chosen to be geometrically similar to hard faced material and they are made either of good weldable steel, or of material with either similar or the same chemical structure as a weld metal.

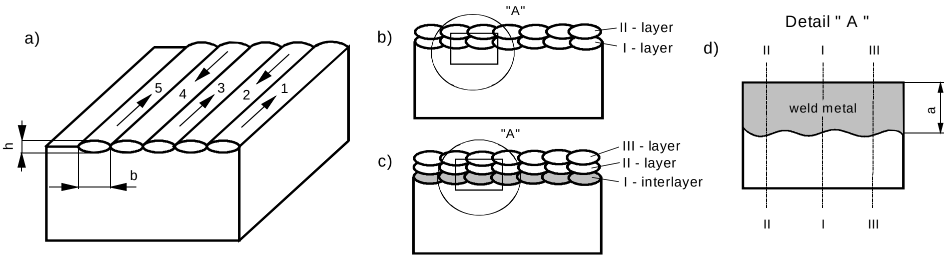


*Figure 3 Order of hard faced layers placement: a - 1$^{st}$ layer, b - 2$^{nd}$ layer, c - 3$^{rd}$ layer, d-metallographic block*

Metallographic samples for hardness, metallographic and tribological tests have been polished and etched with appropriate solvent (nital - 2-4% $HNO_3$ in alcohol, and "czar water" – 20-30 *ml* HCl + 10 *ml* $HNO_3$ + 20-30 *ml* glicerine). Hardness has been measured in accredited Zastava cars laboratory on appropriate devices Zwick (HV) or Knoop (HK), and microstructure has been studied by optical microscope Reichert with maximum magnification of 2000 times [6, 14].

Additional tribological tests are often necessary to decide which filler material and technology should be used. In some of our papers it was pointed significance of these examinations [6, 15-19]. Tribological investigations were done on tribometer TPD-93 at Faculty of Mechanical Engineering in Kragujevac. The aim of these investigations was to determine resistance of the substrate materials to wear, as well as of the deposited coatings - the hard faced layers. In that sense, the "pin-on-disk" contact was realized, where the contact force, the sliding speed, and the lubricant were varied.

Properties of filler materials used in this paper are given in Table 2. These materials are used for hard facing of the surfaces exposed to extremely abrasive wear during the contact of two or more solid bodies. Hard facing is performed with different number of layers - with an interlayer in the case of thicker hard-faced metal, or without an interlayer when one or two layers are deposited (see Fig. 3). For these tribological working conditions, electrodes with increased contents of carbon and carbide forming elements should be used (illustrated in Fig. 2b). This would make them resistant to wear under the given conditions.

*Table 2 Electrodes applied in experimental investigations [20]*

| No | Electrode label Produced by /Standard | Kind of wear | Working temperature | To be used for – hard facing reparation |
|---|---|---|---|---|
| 1. | E10-65 zt - DIN 8555/83 | Metal-metal | T > 500ºC | Cutting edges of tools exposed to increased temperatures |
| 2. | E2 – 60 – DIN 8555/83 | Metal-mineral | Room temperature | Working parts of agricultural machines |
| 3. | E300 k umhülit – DIN 8555 | Metal-metal | T ≈ 500ºC | Parts exposed to intensive abrasion and impact wear |
| 4. | Bilayer plate - Cera metal | Metal-mineral | Room temperature | Intensive abrasion spread mineral particles |

For that reason three types of electrodes have been chosen in these tests [20].

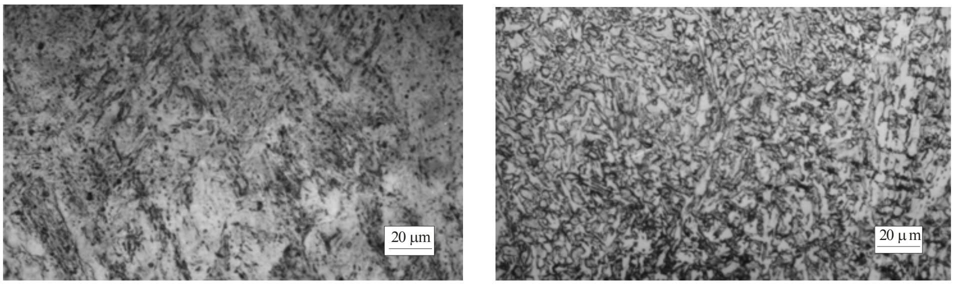
*1. Electrode E10-65 zt - DIN 8555/83*

This electrode is normally used for hard facing and reparation of machine parts exposed to extremely erosive and abrasive wear at high temperatures. The hard faced metal retains good resistance to impact load. Hard faced metal contains Cr, Nb, Mo 5 and W carbides (55%), so it retains high hardness even at temperatures above 600ºC. In hard facing with multi layers, optimal results are achieved with two hard faced layers. For thicker (multilayer) hard faced metal it is necessary to deposit interlayers with chromium-nickel (29/9) or chromium-nickel-manganese electrode (18/8/6). The electrode E10-65 zt has a good application in brick, food, cement, building and mining industry. The usage coefficient is around 190%. The chemical composition of this electrode is: C = 5.5%, Cr = 22%, Nb = 8.0%, Mo = 8.0%, W = 7.0-8.0%, V =1.0%, and the rest is Fe [6, 20].

Alloys used for this type of hard facing with an increased content of carbon and carbide forming elements should not be thicker than a few millimeters because hard-faced metal would crack and peel, especially in conditions of impact loads and thermal fatigue. An example of a multilayer hard-faced metal structure obtained with filler material of this type is given in Figure 4.

Interlayer - HV1 = 453
*Interphase structure*

I layer - HV1 = 660
*Carbides in martensite substrate*



II layer - HV1 = 742
*Martensite fine grain structure*

III layer - HV1 = 772
*Carbides in martensite substrate*

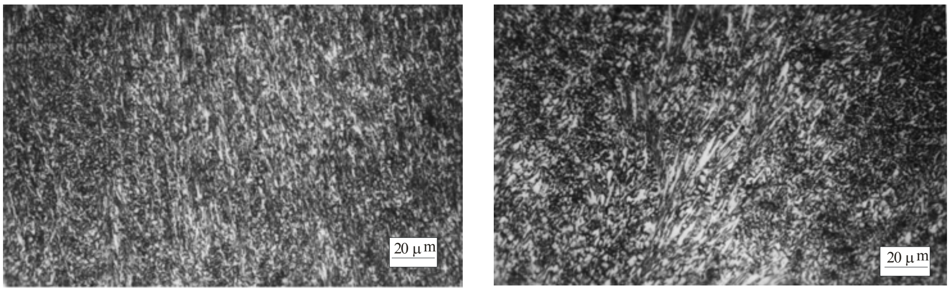


*Figure 4 Microstructure of the hard-faced metal with an interlayer; (Base metal Č1220 – C= 0.12-0.18%, Si= 0.15-0.35%, Mn= 0.30-0.60%; Filler metal - interlayer E29.9 R26 – C= 0.15%, Mn= 1.2%, Cr= 29%, Ni= 9%; Filler metal – hard-faced metal E10-65 zt – C= 5.5%, Cr= 22%, Nb= 8%, W= 7.0-8.0%, V=1.0%) [6]*

*2. Electrode E2– 60 – DIN 8555/83*

This is a high alloy rutile electrode (alloy Cr-Mo). Hard faced layers are resistant to wear and they are also resistant to medium impact wear during exploitation. Hard faced layers can be mechanically processed only by drilling. This electrode is especially suitable for hard facing of parts exposed to friction of metal to minerals. It is used for hard facing of bulldozer bucket knives, excavator bucket teeth, shovel bucket on excavators, parts of conveyers exposed to intensive wear, machines in processing industry etc. Chemical composition of this electrode is: C = 0.7%, Mn = 1.5%, Si = 1.39%, Cr= 6.0%, Mo = 2.0 % and the rest is Fe.

According to our investigations this electrode has shown to be highly resistant to abrasive wear. Working life of thus hard faced parts highly exceeds the working life of original parts [14]. Microstructure of a single-layered hard faced metal is given in Figure 5.

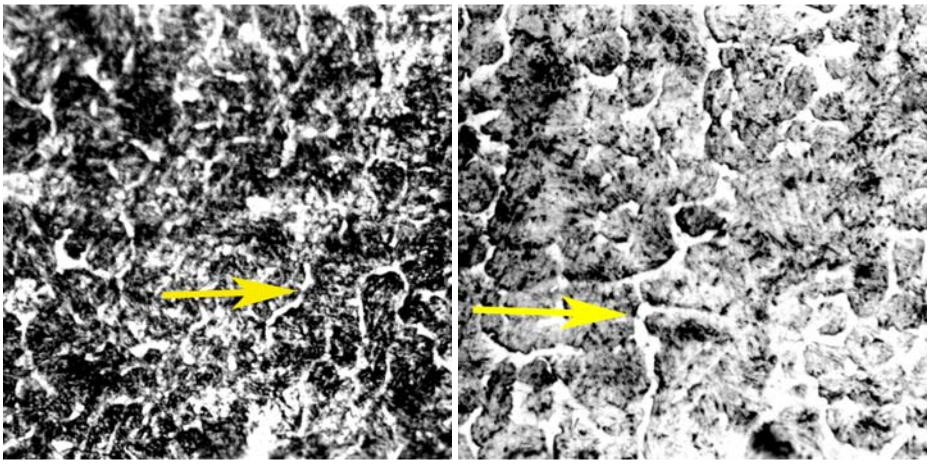


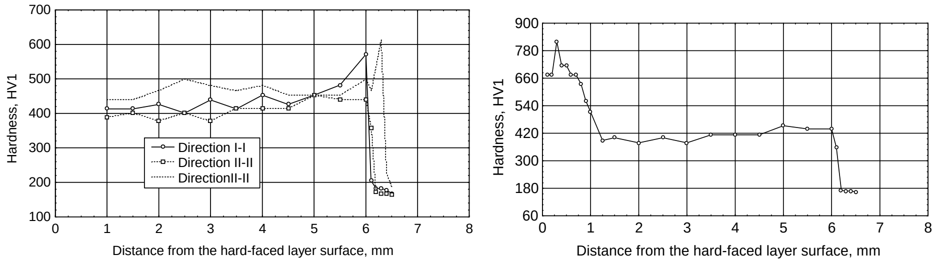
*Figure 5 Microstructure of hard faced layers – martensite with precipitated carbides (shown by arrows) at grain boundaries (500×)*

*3. Electrode E300 k umhülit – DIN 8555*

For parts exposed to impact wear austenite manganese steel should be used (Hadfield's steel), whereas for repair surfacing of such parts one should apply filler material doped with chromium and niobium (1.2% C, 17% Mn, 9.5% Cr i 2.8% Nb), which has higher yield stress than classical Hadfield's steel [6, 15, 18, 20]. Hardness of these alloys after hard facing is, according to our research, ≈ 378-571 HV1 (Fig. 6a), and they have an austenite carbide structure (Figs. 7a, b). When local impact load is applied hardness rises even up to 820 HV1 which is caused by transformation of austenite to martensite in skin deep layers (Fig. 6b).

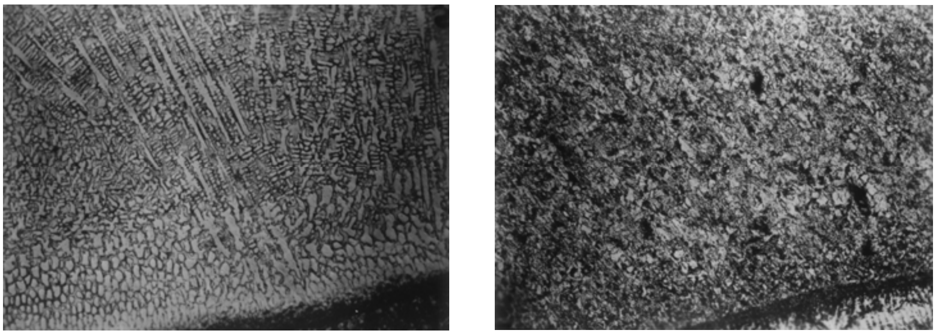
If welded region is exposed either to still pressure in the forming press (1500-2000 daN) or to impact pressure (hammering) the rise of hardness in skin deep layers may be established (Fig. 6b). This increase of hardness is accompanied with the change of microstructure, i.e. beside carbides martensite appears (Fig. 7c). In spite of some difficulties during hardness measurements and microstructural investigations a transformation zone of a width (≈ 1.0 *mm*) was established together with a transformed structure (needles of martensite in austenite grains) [6, 18]. These data may be very important in application of particular mechanical parts in real operating conditions [16, 17, 18, 19].

Abrasive wear caused by dispersed materials is characterized by wear decrease if hardness of working surface is high. One should have in mind that materials with high hardness have low toughness, which is disadvantageous in circumstances when working part is exposed to sudden impact load as when an earth digging machine encounters a stone. This is the reason to develop materials which beside high hardness and strength should have an appropriate toughness.

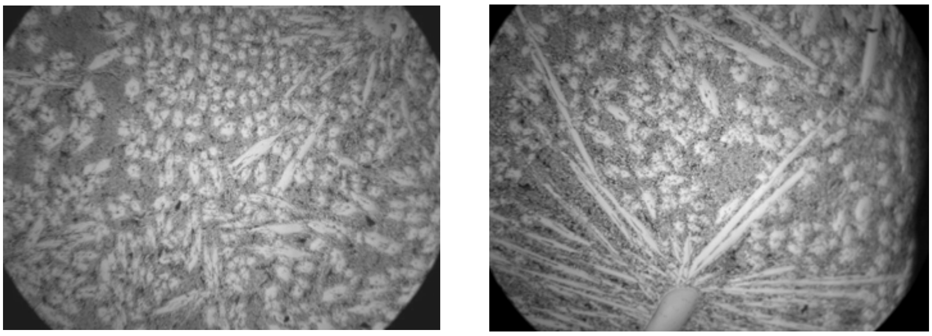


*a) Before forging* *b) After forging*

*Figure 6 Hardness change of hard faced surface doped with austenite manganese Hadfield's steel [6, 17]*



a) Austenite base with excreted carbides – layer I b) Austenite base with excreted carbides – layer II



c) Carbides in martensitic base (500×)

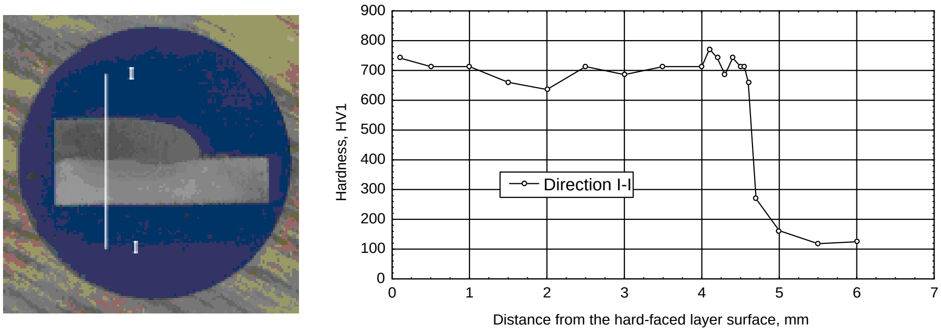
*Figure 7 Microstructure of some weld zones (a, b) Hadfield's steel (FM-Č0561-C= 0.20%, Si= 0.55%,Mn= 1.50%, P=S=0.050%, N= 0.007%; FM-EMn17C10Nb3-1.2%C, 17.5% Mn, 9.5% Cr, 2.8% Nb three passes in two layers; microstructure of skin deep hard faced zones layers after forging (c) [19]*

### *4. Cera-metal double layered welded sheets and plates*

For mentioned reasons a procedure was introduced for processing double layered (two metals) sheets, with the base metal made of low carbide steel sheet thick about 5 *mm*, and a hard faced layer mostly made of materials with hard complex carbides (chrome, nobium, molybdenum). Height of hard faced fragment is about 3 mm. Hard facing should be realized under water since the base metal would be notably deformed (warped). In the present paper tests were performed on Cera-metal double layered sheets (Fig. 8a) [20]. Recommendations of producers specially emphasize following advantages:

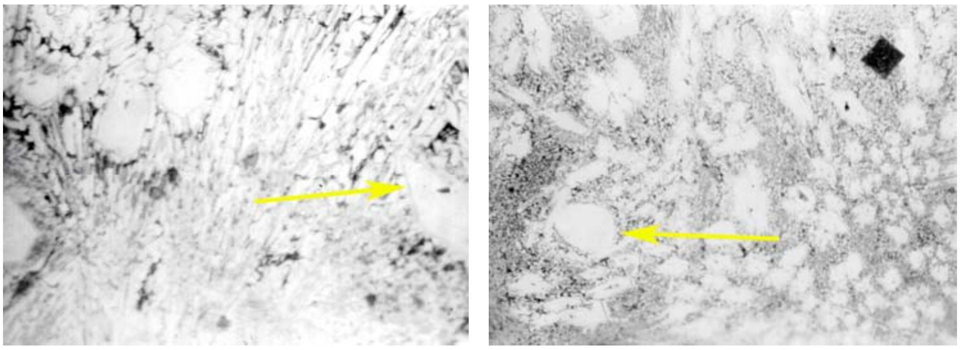
- simple processing of different components (pipes, ducts, tunnels for cement transport etc.
- easy weld joining to steel construction,
- easy cut to prescribed form (plasma cut),
- excellent resistance to abrasive wear (according to abrasive test ASTM 665 endurance is 20 to 30 times longer in relation to usually used materials, and in cement production even 60 times,
- good resistance to erosion wear (erosion test according to DIN 50332),
- good corrosion resistance (due to increased content of chrome)
- thermo stability at elevated temperatures (because of high content of complex carbides),
- very small heat affected zone (HAZ),
- narrow interface between hard faced zone and base material,
- very high carbide concentration,
- possibility to realize austenite-carbide matrix with strong interconnections etc.

Double layered sheets may be obtained as final products on the market [20 – Cera metal, Greece]. Hardness distribution in double layered sheets is shown in Figure 8b, and microstructure of characteristic zones in Figure 9a,b.



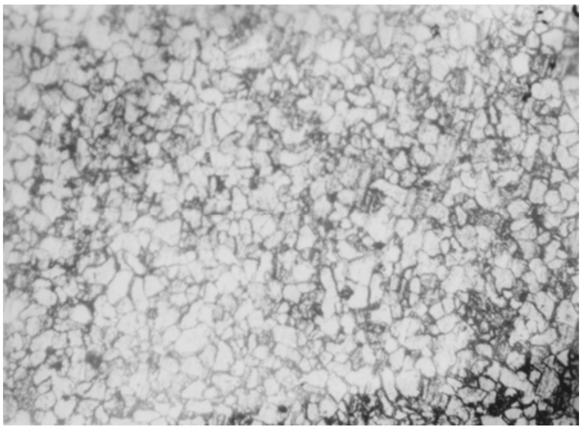
a) b)

*Figure 8 Appearance of double layer hard faced sheet (a) and hardness distribution of hard Cera metal hard faced layer (b) [19]*



a) Martensite base with formed complex carbides (800×)

b) Martensite base with formed complex carbides (200×)



c) Fine grained ferrite structure with small participation of carbides (200×)

*Figure 9 Microstructure of hard faced surface (a, b) and base material (c) double layer hard faced Cera metal sheet [19]*

There is no unanimous agreement on the most favourable type of structure from the aspect of resistance to abrasive wear. Some authors believe that austenite-carbide structure is the most favourable, while according to other it is a martensite-carbide structure [6, 7, 10, 11]. These different opinions are the result of great variety of abrasive wear and wide range of real working conditions.

## Conclusion

Model investigations have shown that, besides the applied technology, the type of filler material has a decisive influence on output characteristics of the hard faced layer. The most important mechanical properties and wear resistance of hard faced metals depend on microstructure and hardness. The paper presents the results of investigations of four different hard faced layers. Depending on both working conditions of the part and dominant type of wear, the most suitable filler material, i.e.

hard facing technology may be chosen. The presented results refer to hardness and microstructure and they indirectly show resistance to wear of working parts. They point out the importance of the right choice of filler materials and hard facing technology, especially for parts exposed to extreme abrasive wear.

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