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V. KAŇA*[#], A. ZÁDĚRA*, V KRUTIŠ***EFFECT OF ALLOYING ELEMENTS ON PROPERTIES AND STRUCTURE OF HIGH CHROMIUM CAST IRONS**

The paper deals with hypereutectic high chromium cast irons. The subject of examination was the effect of various alloying elements (Ti, W, Mo, V) on the size of primary carbides and on the resultant material hardness. Using a scanning electron microscope with a wave dispersion analyser, the carbon content in carbides was established. To determine the other elements, an energy dispersion analyser was used. It was found that both the primary and the eutectic carbides were of the M_7C_3 type and very similar in composition. The carbides always contained Cr and Fe, and also W, Mo, V or Ti, in dependence on the alloying elements used. The structure of materials containing only chromium without any alloying additions exhibited coarse acicular primary carbides. The structure of materials alloyed with another element was always finer. Marked refinement was obtained by Ti alloying.

Keywords: high chromium cast irons, wear resistance, carbides, refinement

1. Introduction

Good wear resistance is required in the operation of many industrial branches. This is frequently case in mineral working, crushers and breakers, various types of mills, etc. In almost every foundry a shot blaster can be found that is used to remove the remains of moulding mixtures from castings exploiting the kinetic energy of grits. It is exactly the protection plates of a suspension-type shot blaster that the experiments described in the present paper were performed on. These are parts exposed to high abrasive wear: their surface is hit by either rebounding particles of the blasting medium or even by particles missing the casting under blasting and hitting the protection plate at full speed. In the present case the abrasive action of the blasting medium was still greater because the respective foundry does not use the usual round steel shot but sharp-edge steel grit, whose edges markedly increase abrasive wear.

High chromium cast irons (HCCI) are a group of materials characterized by high abrasion resistance. This is in particular due to the content of very hard carbides in the structure of the material. The chemical composition, amount and morphology of these carbides are mainly given by the chemical composition of the HCCI.

The paper is oriented to the area of hypereutectic HCCI with a C content of over 3% and the Cr content ranging between 25 and 30%, with focus on verifying the effect of the selected alloying elements (Ti, W, Mo, V) on the size and composition of the formed carbides and also on the resultant mechanical properties of the material as represented by hardness.

2. Materials and methods

Complete protection plates were cast for the experiments, not separate specimens. The plates were then deployed experimentally in the most exposed places of the suspension-type shot blaster in a cooperating commercial cast iron foundry. When they had been worn out and put out of operation, specimens were cut from them for subsequent examination. This was done in an effort to obtain information about the casting of a real component and not from only small laboratory specimens. This protection plate casting of the shot blaster, subsequent to the removal of gating system and following the grinding, is shown in Fig. 1.

The plate dimensions were 480×560 mm, thickness 20 mm, net weight ca 40 kg. The casting process took place in the BUT school foundry. The melting unit was an electric induction furnace with neutral lining, with a maximum capacity of 120 kg. The used moulds were from silica sand bonded via the Alphaset self-setting resin system.

A total of 5 different chemical compositions of HCCI were cast and examined. Individual melts – specimens were denoted with letters. Their composition is given in Table 1. The composition was measured using a Q4 Tasman optical emission spectrometer.

As can be seen from the Table, specimen A (referred to as base material in the following) did not contain, apart from Cr, any further alloying elements. By contrast, specimen B was in addition to Cr alloyed with Mo, W and Cu. Specimens C1 and C2 were in addition to chromium alloyed with Ti (C1 = 0.26% Ti; C2 = 0.97% Ti) while specimen D was in addition to the

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Chemical composition of casted melts – specimens

Specimen	Element [wt.%]									
	C	Si	Mn	Cr	Mo	Ni	Cu	Ti	V	W
A	3.57	0.55	0.64	29.81	0.06	0.29	0.08	0.00	0.07	0.01
B	2.95	0.96	0.94	24.51	1.57	0.27	1.05	0.04	0.06	0.91
C1	3.28	1.07	0.56	28.94	0.05	0.48	0.11	0.26	0.06	0.01
C2	3.38	1.03	0.40	28.16	0.14	0.29	0.13	0.97	0.09	0.01
D	3.26	0.54	0.70	30.46	0.34	0.30	0.07	0.00	0.32	0.13



Fig. 1. Experimental casting – protection plate of shot blaster, with marked place of removal of specimens for further examination

basic content of Cr alloyed with small amounts of Mo, V and W. Only specimen A was exposed to heat treatment at 1100°C / 1 h, with cooling in air and subsequent annealing at 350°C / 2 h and cooling in air. The other specimens were as cast.

Specimens were cut from a place indicated in Fig. 1 by a red rectangle, from which metallographic specimens were prepared and measured for hardness. The Brinell hardness test method was used, ball diameter 10 mm, load 3000 kg. The metallographic specimens were observed using an MTM 406 light microscope and a Zeiss Ultra Plus scanning electron microscope with an Oxford Instruments X-Max EDS detector. The WDS method was applied to establish the exact carbon content in the carbides. Oxford Instruments Wave WDS detector was used. The Vilella etching agent was used to etch the metallographic specimens.

3. Theory section

The greatest effect on the wear resistance of HCCI is the concentration of C and Cr but these materials can also be alloyed with other elements that can significantly influence the resultant properties. These elements include, in particular, Ti, Nb, Mo, W, V, Ni, and others. The aim of such alloying is most often to refine the structure of the material, in particular primary carbides in hypereutectic HCCI [1,2,7], and to form separate or, more frequently, complex carbides with high hardness [3,4,8,9] and, last but not least, to affect the basic metal matrix [5], e.g. in order to get martensite formed in as cast state. In the case of the base material with a C concentration of over 3% and Cr ranging between 25 and 30% without any further alloying elements, the as cast structure is formed by the basic metal matrix with coarse primary and finer eutectic carbides. According to the literature [6,8,9], in both cases the M_7C_3 type carbides are supposed, where M stands for Cr and Fe. The matrix is formed, above all, by austenite oversaturated with carbon and, depending on the cooling rate, possibly also by a minor amount of martensite. If heat treatment takes place subsequently, austenite transforms to martensite, which shows in a marked hardness increase. A minor proportion of austenite remains preserved in the structure. The wear resistance of HCCI then depends on the size of carbides, the primary ones in particular, and on the kind of the basic metal matrix. The fundamental role is here also the material responsible for the wear, i.e. the abrasive, as well as its dynamic action on the surface that is being worn off. In the case of the protection plates of shot blaster and using sharp-edged steel grit, the edges of the abrasive function as a blades and remove microparticles of material from the surface of the protection plates. Thus it might seem that the most appropriate protection plate material is an HCCI with martensitic matrix with the highest hardness possible. But the blasting medium strikes against the protection plate at a considerable speed and if the plate material is too hard, it starts chipping away and the wear rate increases. Also in the case of coarse acicular carbides in the structure of the material the striking particles of the blasting medium make them break up, which leads to increased wear. To manufacture parts worn as given above, HCCI with fine individual carbides embedded in a tough austenitic matrix appear to be the most appropriate.

4. Results and discussion

4.1. Evaluation of metallographic specimens – light microscope

Fig. 2 shows the structure of specimen A, i.e. the base material without any further alloying elements. Clearly visible are the long needles of primary carbides with characteristic hexagonal cross section and a length exceeding even 1 mm. Dispersed among them are small particles of eutectic carbides.

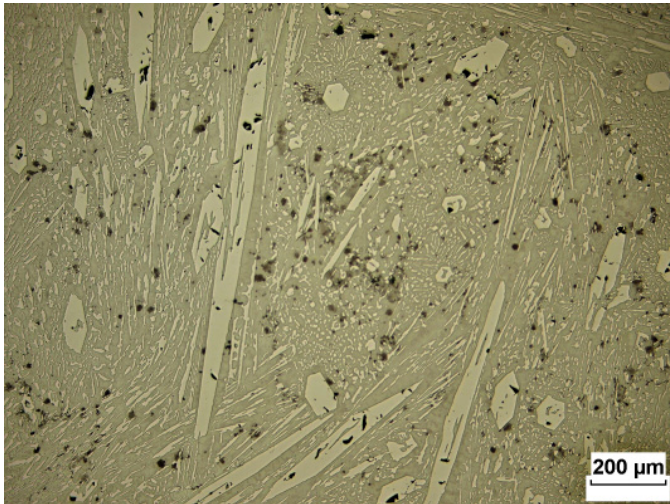


Fig. 2. Microstructure of specimen A (3.09% C; 29.53% Cr)

A comparatively good idea of the primary carbides size and their spatial distribution in the matrix can be formed from Fig. 3. It can be seen here, among other things, that their length is quite often as much as several millimetres. The picture was taken from the central part of the protection plate casting, solidified without the feeder. Thus in course of solidification, primary carbides got precipitate in the thermal axis, which subsequently due to the shrinkage of remaining melt and without the possibility of feeding new melt remained in the just formed shrinkage cavity without matrix and without eutectic carbides.

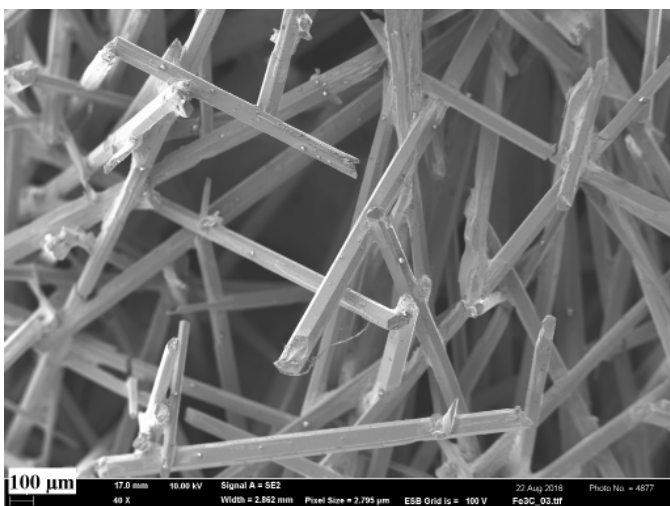


Fig. 3. Size and spatial distribution of primary carbides

From this two figures it then follows that the structure of HCCI without alloying with further elements contains very coarse primary carbides, which are, moreover, comparatively fragile. This fragility is attested by the black points visible in the structure in Fig. 2 and also in Fig. 8. They are cracks in the carbides or voids left by the spalled carbides. This damage appeared in course of operation because, as mentioned above, the specimens were taken from plates that had been deployed in real operating conditions.

Fig. 4 shows the structure of specimen B, which is a specimen with chemical composition according to the literature [8], alloyed with 0.91% W, 1.57% Mo and 1.05% Cu. It can be seen here that there had been a marked structure refinement. The carbides are of elongated shape of 60 – 350 μm in length. Long acicular carbides practically do not appear here and the size of carbides is more uniform on the whole. It needs to be said, however, that the main cause of this may consist in the fact that reducing the concentration of carbon in specimen B to ca 3% and that of Cr to ca 25% (as given in [8]) resulted in a composition close to the eutectic composition.

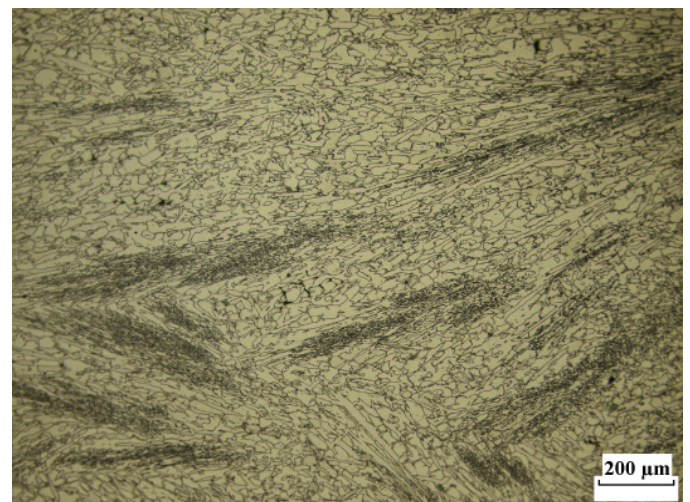


Fig. 4. Microstructure of specimen B (2.95% C; 24.51% Cr; 0.91% W; 1.57% Mo; 1.05% Cu)

Specimen C1 contains 0.26% Ti, specimen C2 0.97% Ti. According to the literature [1,4,7], in HCCI containing Ti there appear fine TiC carbides prior to the liquidus temperature, which subsequently act as heterogeneous nuclei of primary carbides $(Cr, Fe)_7C_3$. The increased amount of nuclei then leads to the refinement of primary carbides. Alloying with Nb works analogously [2]. In Fig. 5 it can be seen that alloying with 0.26% Ti does not lead to any marked structure refinement, although in comparison with the structure of the base material in Fig. 2 a certain reduction in the size of primary carbides can be observed. Acicular carbides are still present in the structure, with their length ranging roughly between 170 and 420 μm. By contrast, in Fig. 6, which shows specimen C2 with a higher Ti content, a pronounced reduction in the size of primary carbides is clearly visible. The occurrence of acicular carbides is markedly suppressed. The size of primary carbides is around 50 – 350 μm.

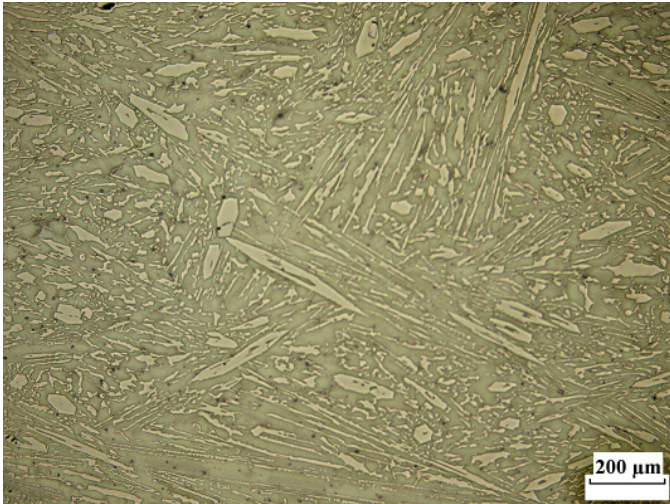


Fig. 5. Microstructure of specimen C1 (3.28% C; 28.94% Cr; 0.26% Ti)

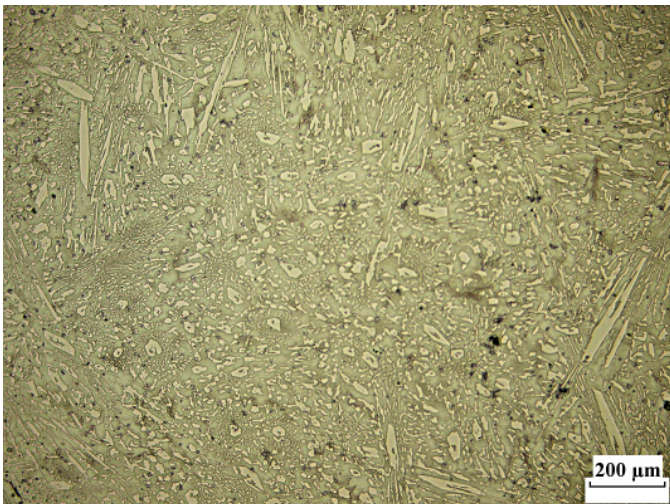


Fig. 6. Microstructure of specimen C2 (3.38% C; 28.16% Cr; 0.97% Ti)

The structure of specimen D is shown in Fig. 7. This specimen is alloyed only with small amounts of Mo, V and W. The

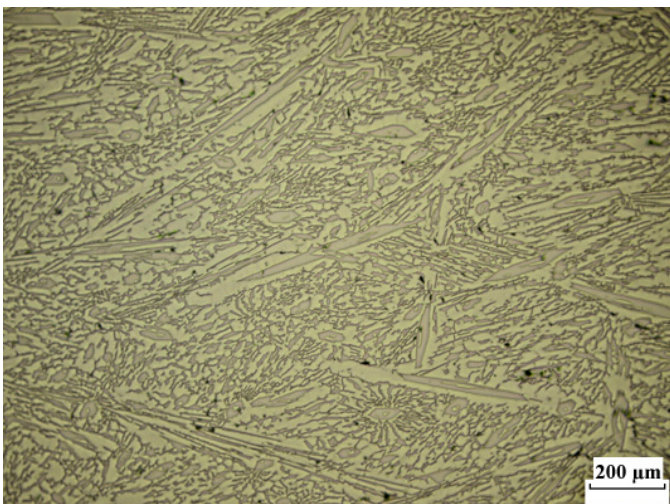


Fig. 7. Microstructure of specimen D (3.26% C; 30.46% Cr; 0.34% Mo; 0.32% V; 0.13% W)

presence of acicular primary carbides is comparatively frequent but, compared to the base material of specimen A, they are more refined. Their size ranges between 80 and 500 μm .

4.2. Evaluation of metallographic specimens – electron microscope

Fig. 8 shows an example of the primary carbide in specimen A. The point P3 indicates the place where the WDS analysis of carbon and the EDS analysis of the other elements were carried out. A total of 3 primary carbides from every specimen were analysed in this way, the average composition is given in Table 2. The composition of eutectic carbides was analysed in the same way, the obtained results are given in Table 3. Fig. 9 shows an example of the eutectic carbide in specimen A, again with marked the place of analysis.

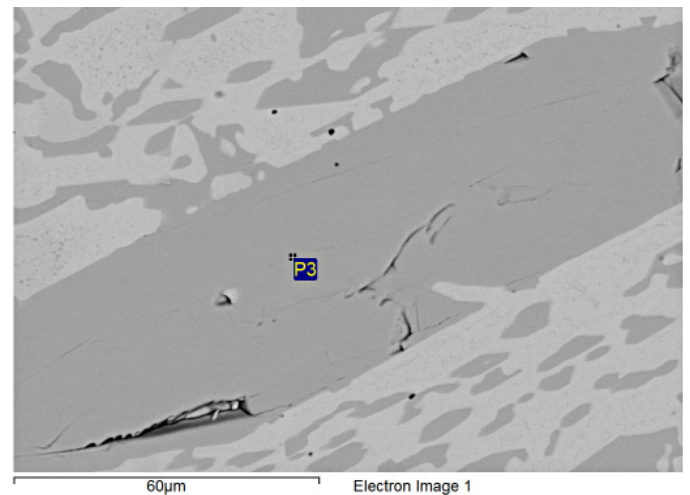


Fig. 8. Primary carbide in specimen A structure

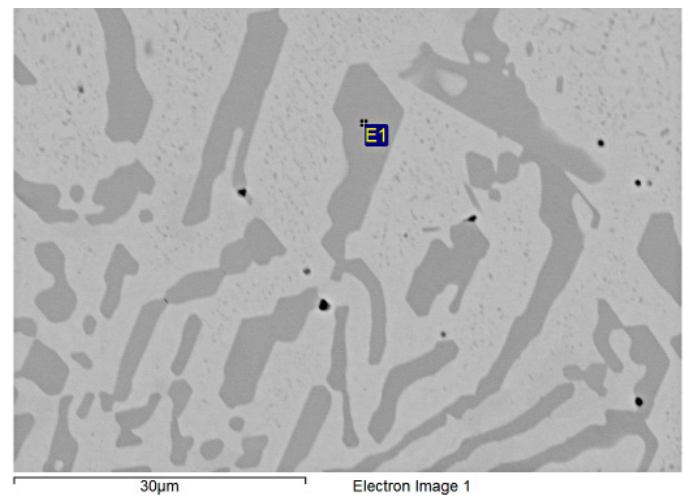


Fig. 9. Eutectic carbide in specimen A structure

It follows from the results given in these Tables that all the analysed carbides, both primary and eutectic, have practically an identical content of C, around 33 at. % on average. From the

TABLE 3

Chemical composition of eutectic carbides in at. %

Specimen	Element [at. %]						
	C	Cr	Fe	Mo	W	V	Ti
A	33.75	44.6	21.7	—	—	—	—
B	31.71	43.1	24.3	0.6	0.3	—	—
C1	33.14	45.4	21.4	—	—	—	—
C2	33.48	44.7	21.3	—	—	—	0.5
D	33.03	46.4	19.9	—	—	0.8	—

TABLE 2

Chemical composition of primary carbides in at. %

Specimen	Element [at. %]						
	C	Cr	Fe	Mo	W	V	Ti
A	34.19	45.5	20.3	—	—	—	—
B	32.40	44.9	21.9	0.5	0.3	—	—
C1	33.20	46.4	20.4	—	—	—	—
C2	33.47	46.1	20.0	—	—	—	0.5
D	32.93	46.9	19.4	—	—	0.8	—

ratio of the concentration of carbon to the concentration of metals forming these complex carbides it can thus be established that the carbides in question are the M_7C_3 type, where M stands for Cr and Fe, possibly also Mo, W, V, and Ti, depending on the alloying additions present in individual specimens.

In the case of the basic composition in specimen A, the carbides are formed by Cr and Fe, with the Cr:Fe ratio being approximately 2.2:1 in the primary carbides, and around 2:1 in the eutectic carbides.

In the case of specimen B, alloyed with Mo, W and Cu, the carbides are formed by Cr and Fe, together with 0.5 at. % Mo in the primary carbides, and 0.6 at. % Mo in the eutectic carbides. Both types of carbide also contain 0.3 at. % W. The Cr:Fe ratio is here lower than in the base material, namely around 2:1 for the primary carbides and 1.8:1 for the eutectic carbides. Copper, of course, does not form carbides, it concentrates in the matrix.

In specimen C1, alloyed with only a small amount of Ti (0.26%), the carbides are only formed by Cr and Fe. In the complex carbides there was no Ti to be found. The Cr:Fe ratio is here 2.3:1 for the primary carbides, and 2.1:1 for the eutectic carbides. In specimen C2, alloyed with 0.97% Ti, the Cr:Fe ratio is the same as in specimen C1, but here Ti was detected in both types of carbide, in an identical amount of 0.5 at. %. The absence of Ti in the complex carbides in specimen C1 can be made clear from Fig. 10. It shows a particle, with the place marked where chemical composition was measured. Results of the measurement are given in Table 4.

As can be seen, this is a composite particle of ca 7 μm in dimension, whose nucleus, some 2 μm in size, is formed by carbonitride Ti(C, N) and the envelope by carbide TiC. Such particles were observed in specimens C1 and C2 in large amounts, both individual and in clusters of over 20 μm in size. In the case of specimen with a low Ti content, all Ti was bonded in these

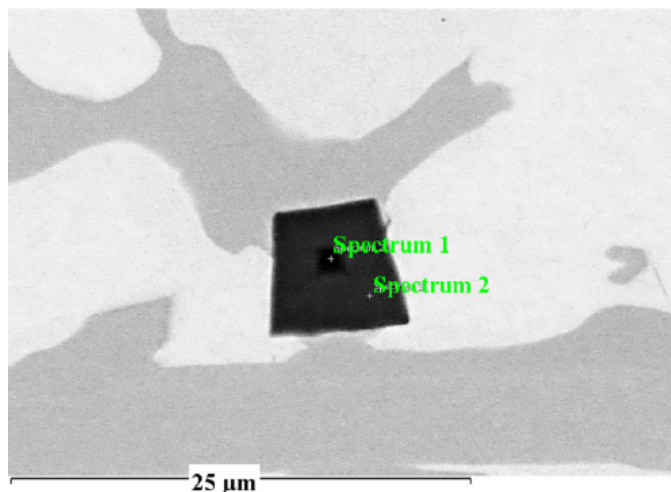


Fig. 10. TiC and Ti(C, N) particles with marked places of chemical composition analyses

TABLE 4

Chemical composition of places from Fig. 10

Place	Element [at. %]								
	C	N	O	Ti	Cr	Fe	Nb	Mo	W
Spectrum 1	26.1	17.0	3.0	49.6	2.6	0.8	0.2	0.4	0.3
Spectrum 2	45.9	—	—	47.7	3.1	1.3	0.3	1.1	0.6

particles, which form already prior to the liquidus temperature, and it could not be detected in neither primary nor eutectic carbides.

In the last specimen, D, alloyed with 0.34% Mo, 0.32% V and 0.13% W, the only alloying element found in the carbides was V, namely 0.8 at. %, identically in the primary and the eutectic carbides. The Cr:Fe ratio was around 2.4:1 for the primary and 2.3:1 for the eutectic carbides.

4.3. Measurement of hardness

All the specimens were also measured for hardness. The results are given in Table 5. They were obtained as the arithmetic average of five measurements. As can be seen, the highest hardness, 621 HB, was, as expected, obtained for specimen A, which had been heat-treated. Specimens B and D exhibit very similar hardness values, 560 and 569 HB respectively. The lowest hardness values were measured for castings alloyed with Ti, specifically 471 HB for specimen C1, and 417 HB for C2.

TABLE 5

Results of hardness measurements by Brinell method

Specimen	A	B	C1	C2	D
HBW	621	560	471	417	569

5. Conclusions

Based on the measurements and analyses performed on castings of protection plates of a shot blaster which were made of hypereutectic HCCI of different chemical compositions, it can be summed up:

- the chemical composition of the primary and the eutectic carbides is very similar,
- in the both types of carbide the ratio of carbon to the sum of metals forming the carbides corresponds to type M_7C_3 carbides,
- in all the specimens the Cr:Fe ratio was in the primary carbides on average some 9% higher than in the eutectic carbides,
- in the base material (3.57% C; 29.81% Cr) without any further alloying additions the coarse primary carbides of acicular shape are formed by 45.4 at. % Cr and 20.3 at. % Fe. Their length exceeds even 1 mm. After heat treatment, the material exhibits a hardness of 621 HB,
- in the material with 2.95% C and 24.51% Cr, alloyed with 0.91% W; 1.57% Mo and 1.05% Cu, complex carbides were formed, containing 44.9 at. % Cr; 21.9 at. % Fe; 0.5 at. % Mo and 0.3 at. % W. The structure is markedly refined, the carbides are of elongated shape, 60 – 350 μm in length. The main cause of the marked refinement will however be the fact that due to the reduced content of C and Cr, in comparison with the base material, the composition came closer to the eutectic composition. The hardness of the material was 560 HB,
- in the material with 3.28% C and 28.94% Cr, alloyed with 0.26% Ti, Ti was bonded as TiC and Ti(C, N), in the form of individual particles (7 μm) or particle clusters (exceeding even 20 μm). Titanium was not found in either primary or eutectic carbides. The primary carbides contained only 46.4 at. % Cr and 20.4 at. % Fe. Some refinement of the primary carbide needles was obtained, to sizes of 170 – 430 μm . The hardness measured for this material was 471 HB,
- in the material containing 3.38% C and 28.16% Cr and also 0.97% Ti, Ti was already detected in both the primary and the eutectic carbides. In the primary carbides it was 0.5 at. % Ti, together with 46.1 at. % Cr and 20.0 at. % Fe. Individual particles as well as clusters of TiC and Ti(C, N) were also observed here. The primary carbides were significantly refined and the occurrence of needles was markedly sup-

pressed. Their length was in the range of 50-350 μm . The hardness value established was 417 HB,

- the material with 3.26% C and 30.46% Cr, alloyed with 0.34% Mo; 0.32% V and 0.23% W, contained primary carbides with 46.9 at. % Cr; 19.4 at. % Fe and 0.8 at. % V. Mo and W were not found in these carbides. The occurrence of acicular primary carbides was comparatively high but they were more refined in comparison with the base material. Their size varied from 80 to 500 μm . The hardness of the material was 569 HB,
- as the most suitable material for protecting plates of the blast machine appears to be the C2 material, i.e. that one containing about 1% of Ti. Primary carbides are significantly refined and lower hardness ensures higher toughness. Another advantage is the relatively low price of Ti compared to e.g. W, Mo or V.

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