NEW CAST IRON ALLOYS WITH HIGH WEAR RESISTANCE AT ELEVATED TEMPERATURES[1]

Gerhard Gevelmann[2]
Werner Theisen[3]

Abstract

New production processes demand a higher wear resistance of tools, especially at elevated temperatures to make the business more profitable and effective. Based on equilibrium calculations new cast iron alloys have been developed. The influence of different alloying elements was investigated before first bulk materials were casted. The materials were tested in respect to their microstructure, hardness, (micro)red hardness, fracture toughness and wear properties (at room- and elevated temperatures) and compared to the standard High-Speed-Steel HS6-5-3 (≈ M3). It turns out that one of the new alloys has equal mechanical properties but superior wear resistance, especially at elevated temperatures, thanks to a tripled carbide content and increased temperature strength of the matrix material.
Key words: New cast alloys; Abrasion; Wear resistance; Mechanical properties.

Resumo

O desenvolvimento de novos processos de produção na busca por maiores lucratividade e efetividade industrais requer uma resistência superior de desgaste das ferramentas utilizadas. Isto se aplica também a processos em alta temperatura. Com ajuda de cálculos de equilíbrio foram desenvolvidas novas ligas de ferro fundido. Essa análise permite prever a influência dos elementos de uma liga antes mesmo da fundição desta. As ligas desenvolvidas foram caracterizadas através de micrografias, medições de dureza e micro-dureza, testes de impacto e de resistência ao desgaste. Os resultados foram comparados aos de um aço rápido (HSS HS6-5-3 ≈M3). Uma das ligas desenvolvidas apresentou propriedades mecânicas equivalentes ao HS6-5-3 tendo, porém, uma resistência ao desgaste superior, especialmente em temperaturas elevadas. A maior resistência ao desgaste tem sua origem no teor triplicado de carbonetos e numa maior resistência mecânica em temperaturas elevadas.
Palavras-chave: Novas ligas de ferro fundido; Resistência ao desgaste; Abrasão; Propriedades mecânicas.

---

1 INTRODUCTION

Often conventional materials do not meet the demands of new applcications anymore. Especially where high wear at elevated temperature occurs, traditional steels have their limits. To improve the productivity of the machines new alloys are required that can withstand the exposure. Considering different processes where the tool material limits the throughput per time, newly developed and customised materials show high potentials in increasing the profit of existing facilities. Tools made out of high speed steels are conventionally used for such applications. They benefit from their high carbide contents and a high strengthened matrix.

This article presents the different steps, which were undertaken to develop new alloys with higher wear resistance at elevated temperatures. Starting from general considerations and definition of the aims over to thermodynamic calculations to test melts and finally bulk materials for specimen production will be presented. Results of mechanical tests performed with both the conventional grade HS6-5-3 (M3) and the new materials, show the potentials of the new material compositions.

2 MATERIALS

The aim of the development was to create new alloy compositions that meet higher demands according to wear and temperature durability. High amounts of hard phases shall ensure good resistance against abrasive and adhesive wear. Additionally a supportive matrix material with high hot strength and red hardness values is necessary.

These aims lead to the development and investigation of the two basic features of microstructure: matrix and carbides.

In the following the basic considerations will be presented for the alloy design, followed by thermodynamic equilibrium calculations before the derived casting compositions are described.

To reach higher carbide contents, the carbon content had to be adjusted and increased. At the same time the amount of carbide forming elements such as vanadium, niobium, molybdenum, tungsten, titanium etc. was raised.

Higher contents of the hard and brittle carbides bear the risk of a reduced fracture toughness.[1-3] To maintain at least comparable mechanical properties, the composition and carbide type distribution had to be changed. The standard grade M3 features mainly M_2C and M_6C type carbides that show a plate-/needle respectively fishbone-like morphology. Also these carbides tend to form networks. Both characteristics strongly deteriorate the fracture toughness.[4] Thus a change to MC-type carbides, which tend to be more round-shaped and are less prone to the formation of networks seemed to be favourable. The superior hardness levels of these phases - about 2800-3000 HV in comparison to 1500 HV (M_2C) and 1800 HV (M_6C)[5] – is also beneficial. In M3 (composition see Table 1) tungsten is known to form M_6C while Mo promotes the M_2C-formation. Tungsten was reduced to about 1.5 wt.-%, Mo to about >3 wt.-%. The molybdenum-content was kept relatively high because of its beneficial effect on hot strength, based on solid solution strengthening. Also it is known to dissolve into MC-type carbides at moderate contents, reducing the risk of M_2C. It is generally known[6-7] that niobium is a strong mono carbide former, which led to the decision to add up to 5 wt.-% to one of the new alloys (HW1).

For a second grade the likewise MC favouring element vanadium was raised in content together with molybdenum to a total percentage (V+Mo) of greater than

10 wt.-%. To achieve a uniform distribution of the carbides in the alloy elements like niobium, titanium and aluminium were added as nucleation agents in small amounts of less than 1 wt.-%. Those elements solidify together with carbon already at a very early stage of casting primarily from the melt. During the further solidification process they act as nuclei for the later forming vanadium-carbides.

To strengthen the matrix especially at elevated temperatures additionally to Mo the element cobalt was added to a content up to 5 wt.-%. The addition of 4 to 7 wt.-% chromium was intended to ensure the hardenability of the material also at thicker diameters.

As most of the above mentioned measures require carbon, the amount of C had to be adjusted, resulting in a carbon content in HW2 of 3.1 wt.-%. Besides the carbide formation the higher contents are needed to maintain the hardenablility of the matrix, which is considered to be ideal at about 0.6 wt.-% C.[5]

Thermodynamic equilibrium calculations were performed using the commercially available software Thermo-Calc© with the database TCFe4, which was developed for iron-based materials. The calculations allowed to see the effect of each single element on the new alloy. Aiming at a matrix carbon content of 0.6 wt.-% at austenitisation temperature the necessary overall C content could be calculated depending on the amount of carbide forming elements and hardening temperature.

This knowledge was used to cast test specimens and do heat treatment investigations at laboratory scale before bigger amounts of bulk material were produced.

Additionally it was possible to calculate phase diagrams of the new materials.

The chemical compositions of the tested materials – M3, HW1 and HW2 – are given in Table 1.

Table 1. Chemical composition of the investigated materials (values in wt.-%)

	C	Cr	Mo	V	W	Co	Nb	Ti	Al
M3	1.20	4.00	4.90	3.00	6.10	-	-	-	-
HW1	1.75	4.00	∑ 3		2.00	3.00	5.00	∑ ≈ 1	
HW2	3.10	7.00	∑ > 10		1.50	5.00	∑ ≈ 1		

As the chemical composition of the new alloys varied significantly from that of standard grades also the heat treatment process had to be adjusted to gain optimal conditions for the application. Considering the necessity to produce large parts holding steps during the heat-up process guarantee low thermal gradient values to avoid thermal stresses. A secondary objective was a low austenitisation temperature to save time and costs in the later serial production. The realisation of elevated application temperatures was supposed to be achieved by applying higher tempering temperatures than normally used for high speed steels (550°C) of above 600°C as it is assumed that softening of the material does not occur as long as the application temperature stays below the tempering temperature.[5]

By those calculations the development costs and time were shortened significantly.

3 METHODS

To characterise the materials and to compare the new grades with the standard M3, tribological and mechanical tests were performed.

Macro hardness tests with a load of 294 N (HV30) at room temperature after a completed heat treatment were performed to evaluate the tempering behaviour of the materials. Therefore the alloys were hardened and then tempered for 2 times 2h at

the same temperature. In steps of 30 K, starting at 450°C up to 640°C the investigations were performed and the hardness taken after the specimens cooled down.

The temperature dependence of red hardness of the matrix was tested by means of micro-hardness tests according to Vickers at temperatures of 580, 600, 620 and 640°C in vacuum using a normal load of 0.49 N (HV0.05) and specimens in hardened and tempered condition.

As investigations on the wear resistance at elevated temperatures were of special interest, grain sliding tests with loose abrasives were performed at different temperatures against Flint (SiO$_2$ – hardness at room temperature 1000-1200 HV)[5] with grain sizes between 50 and 80 μm. The specimen consisted of a ring and a disk, abrasive particles were injected so that the relative rotation of the two parts against each other with the media in between resulted in wear stress of the material. The average mass difference of ring and disk - before and after the test - in relation to the performed test path and the specimen´s density was taken as the wear rate. The wear resistance is the reciprocal value. The tests were performed at room temperature, 450 and 550°C.

The fracture toughness was determined as tools often have to withstand higher mechanical loads and stresses in application and should not fail due to cracking. In four point bending tests Charpy notched specimen with a length of 80 mm and 5 mm thickness were oscillated until a crack was initiated. The force needed to fully crack the specimen was measured to determine the critical fracture toughness of the hardened and tempered materials.

The carbide contents were investigated using binarised light microscope pictures and applying an automatic point analysis with a point distance of 3 μm. The results are the average of five measurements at five different polishing depths.

A comparison of the M3 to the newly developed alloys should show the potential of the new materials.

4 RESULTS AND DISCUSSION

4.1 Thermodynamic Equilibrium Calculations

Figure 1 shows the obtained phase diagrams for the standard grade HS6-5-3 (M3) as well as for the two new alloys HW1 and HW2. For easier orientation the carbon level of ach material is marked with a vertical line.

Following the concept of changing the carbide type in the as cast material towards MC, the fields where only Austenite and MC occur are most relevant. Both HW1 and HW2 show such a field over a comparably wide C- and T- range. M3 always contains amounts of the M$_6$C carbide. As the diagrams show, the range for the hardening treatment is rather comfortable according to a possible temperature range at given C-level, for the HW1 even more than for HW2 where the A+MC field is more narrow. The calculations showed that austenitising temperatures below 1200°C are sufficient to obtain a matrix carbon content of about 0.6 wt.-% and a resulting good hardenability. Additionally it was revealed that cobalt remains completely in the matrix and does not participate in the formation of hard phases.
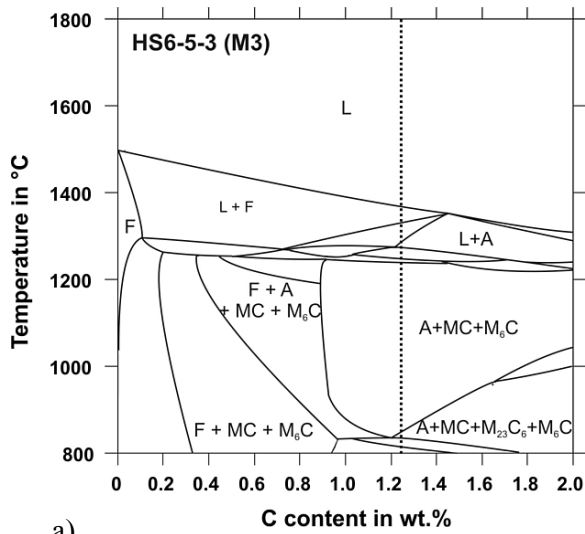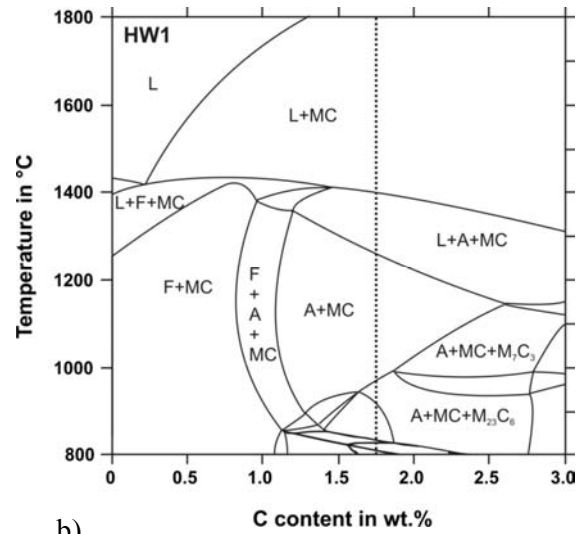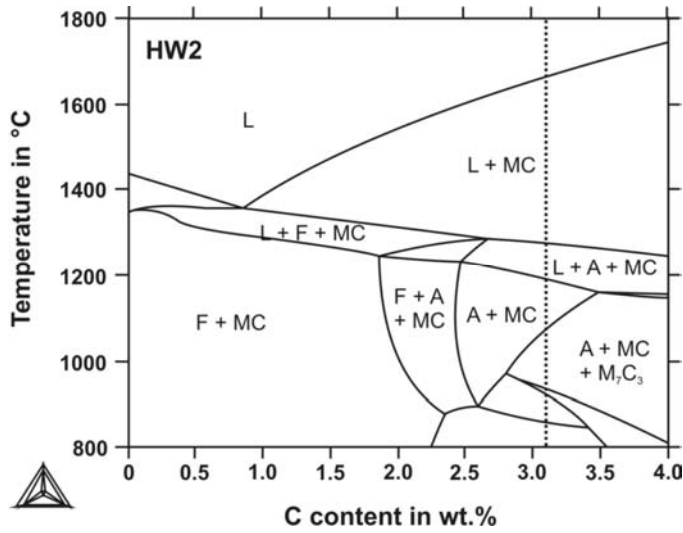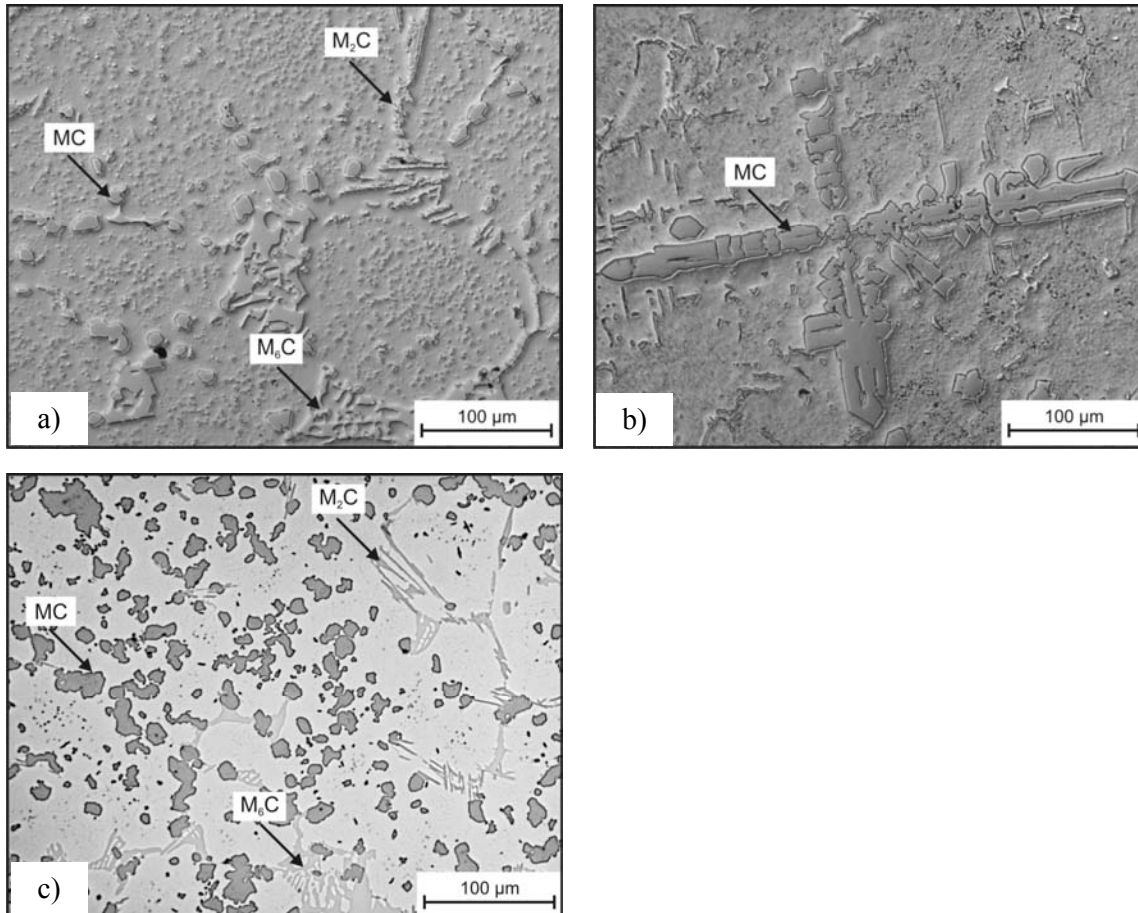
Figure 1. Calculated phase diagrams of a) HS6-5-3 (M3), b) HW1 and c) HW2.

4.2 Microstructure

The as cast microstructures of the three materials are shown in Figure 2.

Figure 2. Microstructures of the materials in as cast state, a) HS6-5-3 (M3), b) HW1 and c) HW2.

Whereas the HS6-5-3 (M3) mainly shows needle/plate like M_2C and fishbone shaped M_6C carbides that form network structures, accompanied by few smaller and round shaped MCs, the new alloys show a completely different microstructure.

The effect of the high niobium content (5 wt.-%) in HW1 is very obvious. Rather blocky, long ranging MC carbides with an extension up to 500 μm solidify from the melt. Similar results have been reported in.[8] As the time until further phases besides the primary MC solidify is rather long – as can be seen from the phase diagrams (Figure 1) - , the NbC can grow to such extensions. Though, the aspired reduction of the eutectic M_2C and M_6C carbides was successful. As picture c) shows, the microstructure of the HW2 mainly contains uniformly distributed MC carbides and small amounts of M_2C and M_6C. The size of the hard phases is about 10-50 μm and network structures cannot be found.

As EDX-investigations revealed, the MC- carbides of M3 and HW2 basically contain vanadium and significant amounts of molybdenum. They are round shaped and uniformly distributed in the matrix. Clusters or networks like in the other two materials do hardly occur. This is the result of the addition of elements such as niobium, titanium and aluminium that start solidifying as MC type carbides from the melt already at high temperatures. On these nuclei later setting phases like VC can grow. The amount of carbon in the rest melt is reduced, which does not allow eutectic phases (ferrite) to form. The alloy composition of HW2 therefore only contains very

low amounts of M_2C and M_6C structures. The formation of network structures, which would reduce e.g. the fracture toughness, could also be prevented.

Comparing the amount of carbides, the effects of the different modifications in the alloying systems become significant. Measurements showed about 9 vol.-% in HS6-5-3 (M3) with a carbon level of 1.2 wt.-%, there from about 8 % as M_2C and M_6C, 1% MC, which is in agreement with other´s investigations.[7] The alloy HW1 with about 1.75 wt.-% C already contains about 11 vol.-% of hard phases, nearly all of them MC type carbides. The aim of a significant increase of wear resistant hard particles was reached by HW2. A total measured amount of about 25 vol.-% carbides, mainly of MC type, only a few M_2C and M_6C, was realised in the new alloy. The increase in carbide forming elements such as vanadium and molybdenum together with carbon (3.1 wt.-%) enabled this tripling in carbide content in comparison to the standard material.

4.3 Hardenability and Red Hardness

As Figure 3 presents especially the new grade HW2 reveals superior hardening-tempering properties. At all temperatures the material shows about 80 HV higher hardness level as the competitors. Even after tempering for 2h at 640°C a composite hardness of about 680 HV30 is reached. The two other alloys are at a same level over a long temperature range. At 640°C the standard HS6-5-3 (M3) shows even a higher hardness level than the new alloy HW1. After this result it was decided not to investigate the HW1 further as both, the microstructural investigations as well as the hardness results, did not meet the demands. The following results therefore only contain values for the M3 and the HW2.
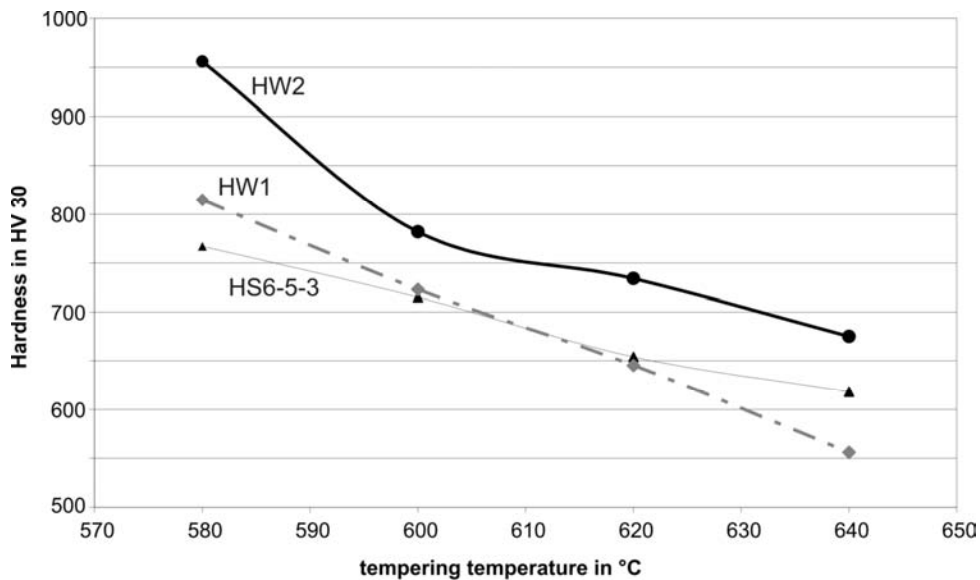

Figure 3. Macrohardness after hardening and tempering at different temperatures.

After proving the hardenability of the new composition HW2, further investigations according to the temperature durability were performed. Especially the matrix material was of interest as a soft core does not support the carbides, which would result in bad wear resistance. The results of the microhardness measurements of the matrix material at temperatures up to 640°C are shown in Figure 4.
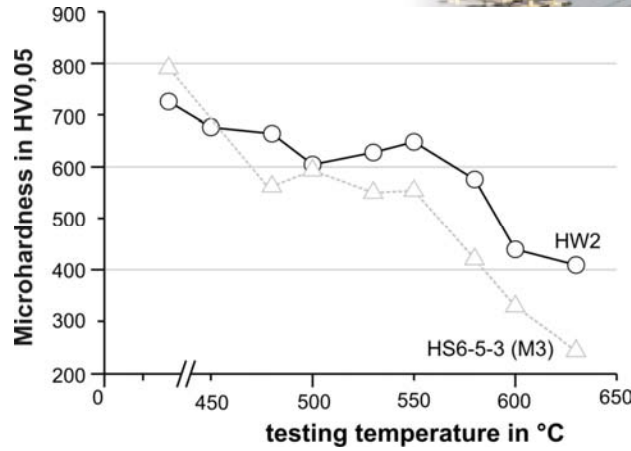
Figure 4. Microhardness measurement of the matrix.

Though the standard material shows superior values at room temperature, HW2 reveals its advantages at higher temperatures. At 550°C (which is the aspired maximum tool temperature in service) even a slight secondary hardening maximum is visible with about 630 HV0.05 whereas the HS6-5-3 is much below 600 HV0.05. At the maximum testing temperature of 640°C the HW2 matrix still gives more than 400 HV0.05 in comparison to the very soft standard matrix with only about 250 HV0.05. The carbides rather keep their hardness at the tested temperatures[6] but the matrix tends to soften with increasing heat due to the reduction of bracing of carbon in the martesitic structure. HW2 in opposite shows higher hardness values at elevated temperatures. Here the effect of solid solution strengthening of cobalt and molybdenum becomes relevant. They avoid a strong softening of the matrix at higher temperatures.

4.4 Wear Properties

The above mentioned results show their relevance when performing wear tests. Whereas at room temperature HW2 is only slightly superior to the HS6-5-3 (M3) and rather equal at 450°C, the potential of the new material becomes obvious at 550°C (Figure 5). Here the wear resistance is more than double of what the standard grade can offer.
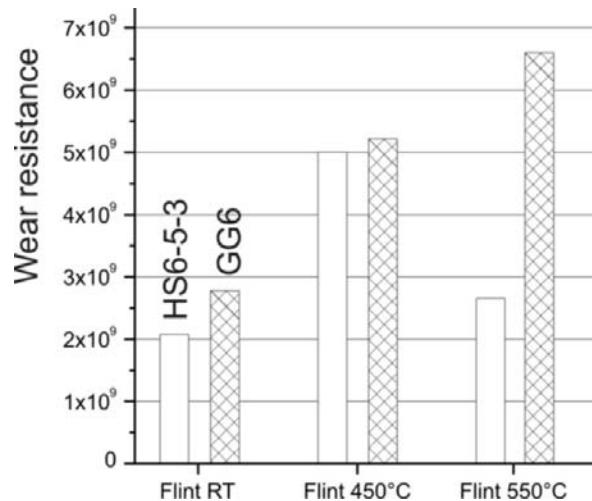

Figure 5. Wear resistance against loss abrasive at different temperatures.

The measured wear resistance of HW2 increases with increasing temperature. This seems odd, since the matrix hardness decreases at the same time as Figure 4 shows. To interpret these findings, one has to keep in mind that not only the tested materials but also the used abrasive softens at higher temperatures.[5]

Hence the ratio between the two alloys is of importance, not the overall value of wear resistance. The three times higher carbide content as well as the higher hardness of the major hard phase MC (2800-3000 HV)[5,7] in HW2 in comparison to the M_2C (1500 HV)[5,7] and M_6C (1800 HV)[5,7] in the standard material HS6-5-3 (M3) can protect the material against abrasion. When applying higher environmental temperatures the difference between the two alloys is even more significant as now the matrix becomes more and more important. As the results of the red hardness testing revealed, the HW2 matrix stays much more stable especially at the temperature range around 550°C, which is tested here. Not only that the matrix itself is more wear resistant but is also supports the carbides in a way that they can show their full potential as protection against the abrasive particles. The elements cobalt and molybdenum act as solid solution strengtheners, an effect that is still relevant at high temperatures in opposite to the martensitic hardening, which resolves magnificently in comparison.[5,9,10]

The combination of a higher carbide content and a hot strengthened matrix results in the superior wear resistance of the new alloy HW2.

4.5 Fracture Toughness

The fracture toughness values of the standard and the new material in the hardened and tempered state are of the same level, both about 33 to 34 MPam$^{1/2}$ (Table 2).

Table 2. Fracture toughness (K_{Ic}) values of HS6-5-3 (M3) and HW2

	Fracture toughness (K_{Ic}) in MPam$^{1/2}$
HS6-5-3 (M3)	33
HW2	34

This reveals that the new material, although the carbide content was tripled, did not fall back significantly in its mechanical properties even though normally such an increase in the content of brittle phases leads to a reduction of fracture toughness.[1-3]

The change from mainly needle/plate like M_2C and fishbone like M_6C carbides to round shaped MCs results in good fracture toughness values. The comparably small mono carbides do not show the tendency to break under load as the other types do due to their length-width ratio nor have sharp edges where stress concentration takes place, which both leads to crack initiation.[7] Additionally the uniform distribution of the hard phases within the matrix results in the advantage[2] that a crack has to propagate through the more ductile matrix and cannot just run along the carbide networks. This means a loss of fracture energy and a reduction of progress speed through the specimen.

5 CONCLUSIONS

The development of new cast iron materials has been described. First general influences of different alloying elements were combined and based on thermodynamic equilibrium calculations different test alloys casted. The resulting microstructures showed in one composition pretty blocky MC type carbides with a

longitudinal extension of up to 500 µm. The second test melt contained a uniform distribution of mainly MC type carbides with few amounts of M_2C and M_6C hard phases. The different testes properties, especially of the second alloy, HW2, were equal – K_{Ic} – or superior to a standard high speed steel HS6-5-3 (M3), even though the carbide content was tripled.

In total a new high wear resistant steel with superior properties compared to a standard grade could be developed, tested and prepared for implementation as tool steel for high wear and high temperature applications.

REFERENCES

1   Broeckmann, C.: Bruch karbidreicher Stähle - Experiment und FEM-Simulation unter Berücksichtigung des Gefüges. Ruhr-Universität Bochum, Germany, Doctoral Thesis, (1994).

2   Berns, H. ; Nguyen, Chuong van: A new microstructure for PM tooling material. In: Metal Physics and Advanced Technology 16 (1996), p. 693–706.

3   Hinz, H. F.: Einfluss der Karbidmorphologie auf die Warmfestigkeit von Schnellarbeitsstahl. Ruhr-Universität Bochum, Germany, Doctoral Thesis, (1999).

4   Karagöz, S. ; Riedl, R. ; Gregg, M.R. ; Fischmeister, H. F.: Die Rolle des M_2C-Carbides in Schnellarbeitsstählen. In: Sonderbände der Praktischen Metallurgie (1983), p. 369–382.

5   Berns, H.; Theisen, W.: Ferrous Materials – Steels and Cast-Iron. Berlin : Springer (2008).

6   Gale, W. F.; Totemeier, T. C.: Smithells metals reference book. 8. ed. Amsterdam: Elsevier/Butterworth-Heinemann (2004).

7   Brandis, Helmut ; Gümpel, Paul ; Haberling, Edmund ; Weigand, Hans H.: Beitrag zum Einfluß einiger Legierungselemente auf die metallkundlichen Eigenschaften von ledeburitischen hochchromhaltigen Kaltarbeitsstählen. In: Thyssen Edelstahl Technische Berichte 7 (1981), No. 2, p. 221–230.

8   Theisen, W.; Siebert, S.; Huth, S.: Wear resistant steels and casting alloys containing niobium carbide. In: Steel Res Int (Steel Research International) 78, No. 12 (2007), p. 921-928.

9   Kwon, H. ; Kim, C. M. ; Lee, K. B. ; Yang, H. R. ; Lee, J. H.: Effects of Co and Ni on secondary hardening and fracture behavior of martensitic steels bearing W and Cr. In: Metallurgical and Materials Transactions A, No. 29 (1998), p. 397–401.

10   Wang Rong ; Andrén, H.-O. ; Wisell, H. ; Dunlop, G. L.: The role of alloy composition in the precipitation behaviour of high speed steels. In: Acta Metallurgia et Materialia 40 (1992), No. 7, p. 1727–1738.