EFFECT OF NIOBIUM AND VANADIUM AS AN ALLOYING ELEMENT IN TOOL STEELS WITH HIGH CHROMIUM CONTENT

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Abstract There is a common wish to increase the wear resistance of cold work steel. The possibility to improve wear resistance by the addition of more alloying elements is limited, due to the loss of toughness. Therefore one tries to extend the weight percentage of alloying elements like niobium and vanadium which form very hard carbides.

This paper will explain to which extent niobium and vanadium are suitable for this purpose and which other effects have to be considered.

Keywords: Cold-work, tool steels, alloying

INTRODUCTION

Cold work tool steel contains up to about 25% carbide forming alloying elements. When these high alloyed steels are conventionally manufactured, they are not ductile and can only be used for cast tools. An example for this double worm extrusion cylinders in plastic manufacturing machines, made of an alloy with 2.8% C and 25% Cr (W.-Nr. 2593). With the commercial introduction of powder metallurgy (PM) these alloys became ductile. At the same time in cold work tool steels the chromium content was partly substituted by alloying elements that form harder carbides, like vanadium or niobium (see Fig. 1). This paper describes the action of vanadium and niobium as alloying elements in tool steels with higher chromium content.

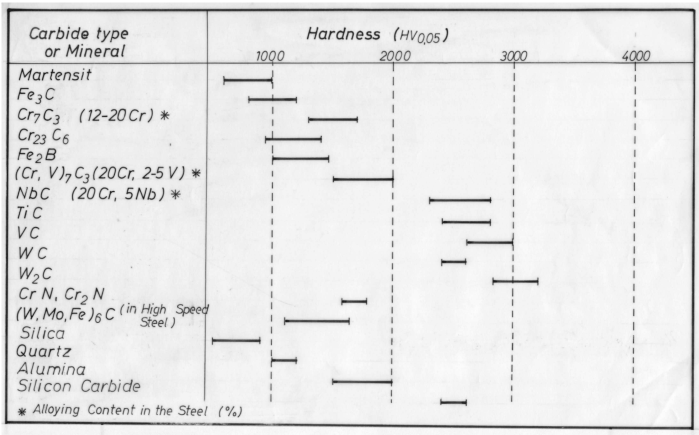

Figure 1. Hardness of carbides in tool steels and of other hard substances [1].

ACTION OF VANADIUM AND NIOBIUM IN THE MELT AND AT GAS ATOMIZING OF TOOL STEELS WITH HIGHER CHROMIUM CONTENT

Vanadium is by far the most used element to improve wear resistance in tool steels. Today there are several V-alloyed tools steels up to 18% vanadium [2] in the market. In these steels the wear decreasing vanadium rich carbides are either formed eutectically at the solidification of the residual melt or in isolation at approximately the same time as the eutecticum [3]. Though the formation of primary vanadium carbides, that make the melt viscous, is possible [4], there is no information available about difficulties of pouring or gas atomizing melts with higher vanadium content.

Contrary to vanadium, higher contents of niobium cause considerable difficulties in the melt. In melts containing more than about 2.5 wt% niobium,

niobium carbides directly precipitate at higher temperatures in form of cubic or octaeder faced crystals Figures 2 and 9, before the ferritic crystallisation of the melt starts. By increasing amounts of primary NbC-crystals, the melt becomes more and more viscous and pulpy. Due to the viscosity, melts with more than about 3% niobium cannot be poured in tool moulds and cannot be gas atomized. For this reason the niobium content in tool steels is limited today to about 2%.

There are many attempts to improve the poor solubility of niobium in the melt. But until now no experiment has been successful and satisfactory [6]. The only possibility to increase wear resistance by higher niobium content is hard facing of tools by welding electrodes or by laser alloying.

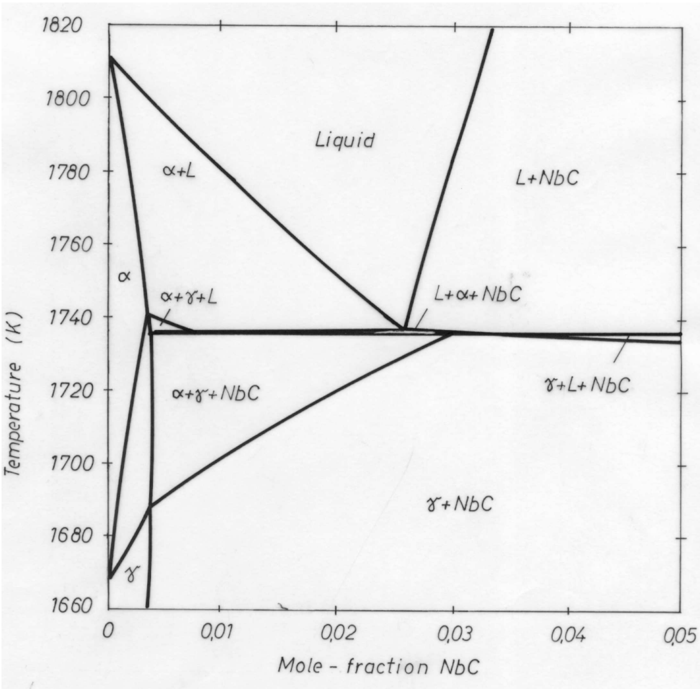

Figure 2. Ternary system Fe-Nb-C. Calculated section Fe-NbC [5].

SOLUBILITY OF VANADIUM AND NIOBIUM AT HEAT TREATMENT

The solubility of alloy carbides at austenitizing temperature and their precipitation at higher tempering temperatures causes secondary hardness. Contrary to vanadium carbides, niobium carbides have a very poor solubility at hardening temperature Fig. 3. At 1000 ℃only 0.02 wt% of niobium are soluble in austenite Fig. 4. This means: niobium can hardly contribute to the secondary hardness of tools steels. Therefore niobium cannot completely substitute vanadium which is essential to bring about secondary hardness.

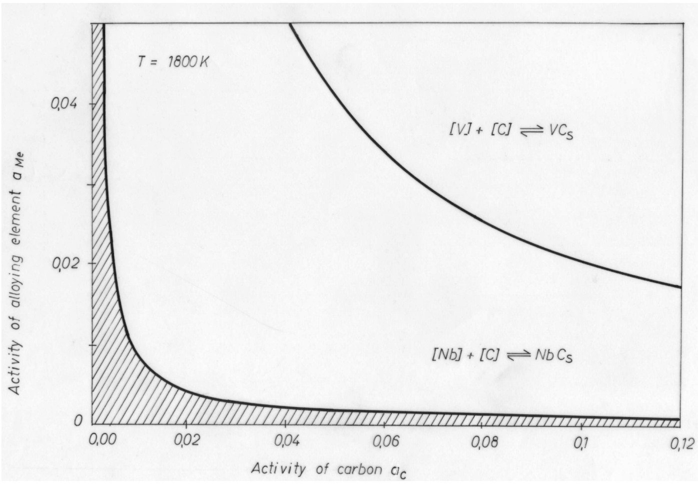

Figure 3. Calculated solution curves for Nb and V-carbide in iron melts at 1800K [7].

Because of the low solubility, niobium carbides remain rather unaffected at austenitizing temperature. For this reason NbC reduces the growth of the austenite grain size at hardening temperature and enables higher hardening temperatures.

MICROSTRUCTURES IN TOOL STEELS WITH HIGH CHROMIUM CONTENT AND ADDITIONS UP TO 4 WT% VANADIUM OR NIOBIUM

To show the influence of vanadium an niobium on the microstructure and on the carbide hardness of chrome alloyed tool steels, some laboratory

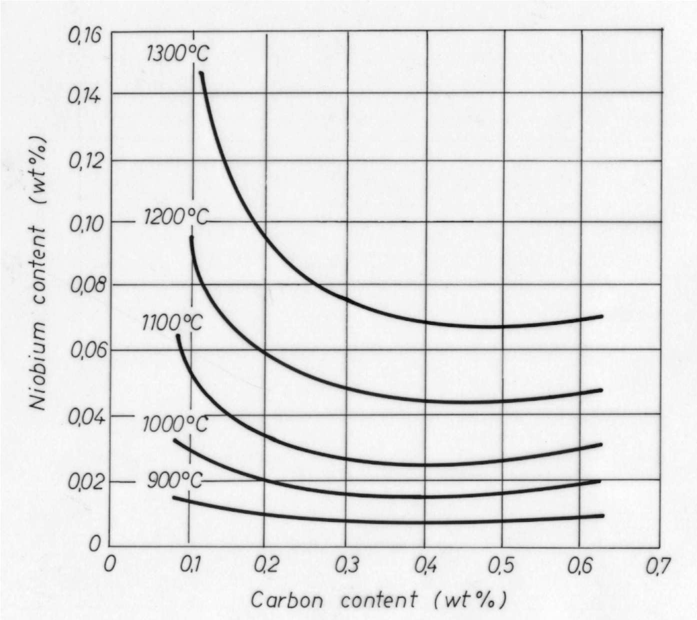

Figure 4. Solubility of NbC in austenite [8].

melts were cast. Table 1 shows the analysis of these test melts with about 20% Chrome and additions of 2 and 4 wt% vanadium or niobium. The test melts had a weight of 5 kg and were poured in ceramic moulds of 60 mm square. To reduce the cooling rate of the melts, the moulds were preheated at 1000 ℃and embedded in sand.

Figure 5 shows the microstructure of a V- and Nb-free cast alloy W.-Nr. 2593 taken from an extrusion cylinder. All carbides in the microstructure of Fig. 5 are of the type Cr_7C_3 as has been proven by X-ray structure analysis (see Table 2).

By the addition of 2 or 4% vanadium, the carbide type in the microstructure remains unchanged Cr_7C_3 (Fig. 6). Vanadium carbides of the type MC have not been detected (see Table 2). It is to assume that the added vanadium is completely dissolved in chromium carbide.

On the other hand the addition of niobium changes the microstructure completely. After alloying niobium the structure shows two types of carbides, the chromium rich carbide Cr_7C_3 and the niobium carbide NbC (see

Table 1. Chemical composition of chromium alloyed castings with additions of vanadium or niobium

Test heat №	Chemical Composition [wt%]								
	C	Si	Mn	P	S	Cr	Mo	V	Nb
1A	2,42	0,62	0,56	0,011	0,023	19,50	0,52	1,90	0,01
1B	3,28	0,56	0,63	0,011	0,024	19,50	0,50	4,01	0,01
2A	2,23	0,63	0,28	0,014	0,024	19,15	0,53	0,07	2,03
2B	2,85	0,68	0,57	0,015	0,026	19,20	0,51	0,07	4,04
W.-Nr. 2593	2,80	0,63	0,50	0,013	0,028	22,40	0,47	0,33	0,02
1A + S	2,58	0,68	0,63	0,012	0,072	19,25	0,51	1,85	0,020
2A + S	2,28	0,90	0,57	0,014	0,095	19,90	0,50	0,36	2,08

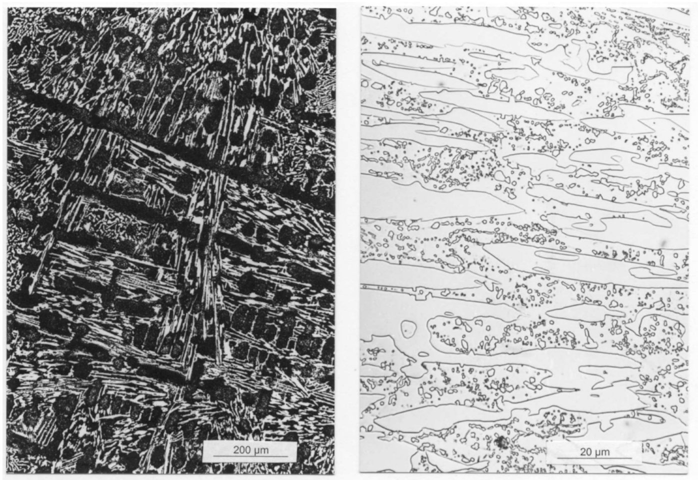

Figure 5. Microstructure of the cast alloy W.-Nr. 1.2593 (2.8% C; 25% Cr).

Table 2). In the alloy with about 2% Nb (alloy 2A) the niobium carbide has an entectic appearance, but a crystallographic solidification of these niobium carbides can be recognized in Fig. 7. These NbC must have been formed between the begin of solidification and the eutectic temperature where the residual melt decomposes to chromium carbide and austenite. Figure 8 shows the same microstructure etched and relief polished. One can clearly

Table 2. Carbides in the tested cast alloys in the annealed condition

Test heat №	Amount of undissolved carbides [wt%]	Types of carbides [wt%] determined by X-ray structure analysis
1A	29,1	100% Cr_7C_3
1B	35,9	89% Cr_7C_3 , 11% $(Cr, Fe)_7C_3$
2A	26,6	34% NbC, 63% Cr_7C_3, 3% $(Cr, Fe)_7C_3$
2B	28,7	26% NbC, 24% Nb_6C_5, 30% Cr_7C_3 , 20% $(Cr, Fe, Mo)_7C_3$
W.-Nr. 2593	27,2	66% Cr_7C_3, 34% $(Cr, Fe)_7C_3$
1A + S	30,0	82% Cr_7C_3, 17% $(Cr, Fe)_7C_3$
1B + S	26,3	19% NbC, 64% Cr_7C_3, 17% $(Cr, Fe)_7C_3$

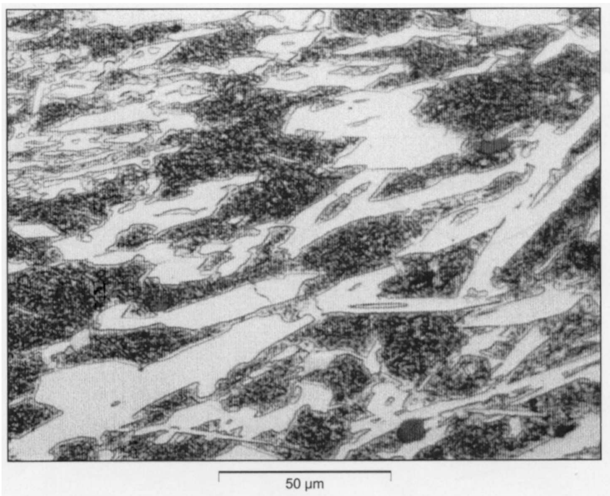

Figure 6. Microstructure of the cast alloy 1B (3.3% C; 19.5% Cr; 2.0% V).

distinguish the two carbide types. The hard NbC is distinctly elevated while the softer Cr_7C_3 is more blurred in the background.

In the melt with 4% niobium, the niobium carbide has another shape. At this content niobium carbide directly precipitates at higher temperatures in the melt before the ferritic solidification of the alloy starts. By this way the NbC could here develop en exact crystallographic cubic or octaeder form

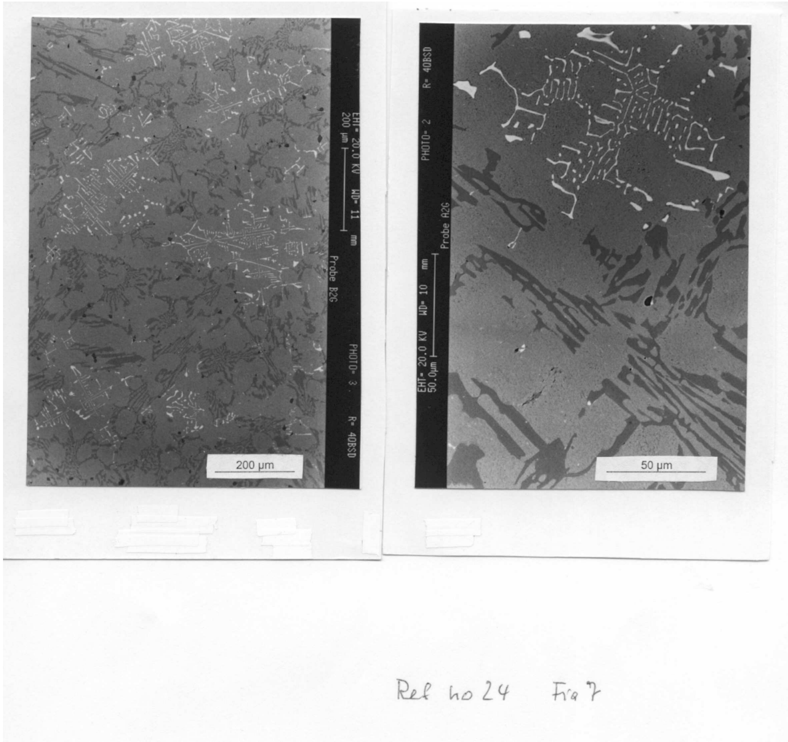

Figure 7. Microstructure of the cast alloy 2A (2.3% C; 19.2% Cr; 2.0% Nb). Bright carbides NbC, dark carbides Cr_7C_3 (SEM photo).

as Fig. 9 shows. The cubic niobium carbides are random distributed in the structure. Some carbides have grown up to about 50 µm,(Fig. 9).

HARDNESS OF THE CARBIDES IN CHROMIUM ALLOYED TOOL STEELS WITH ADDITION OF UP TO 4 % VANADIUM OR NIOBIUM

The carbides in the test melts were mostly big enough to measure the micro hardness with a load of 50 g. In the V and Nb free alloy W.-Nr. 2593 (Table 1) the chromium carbides had an average hardness of 1499 HV with a standard deviation of 223 HV.

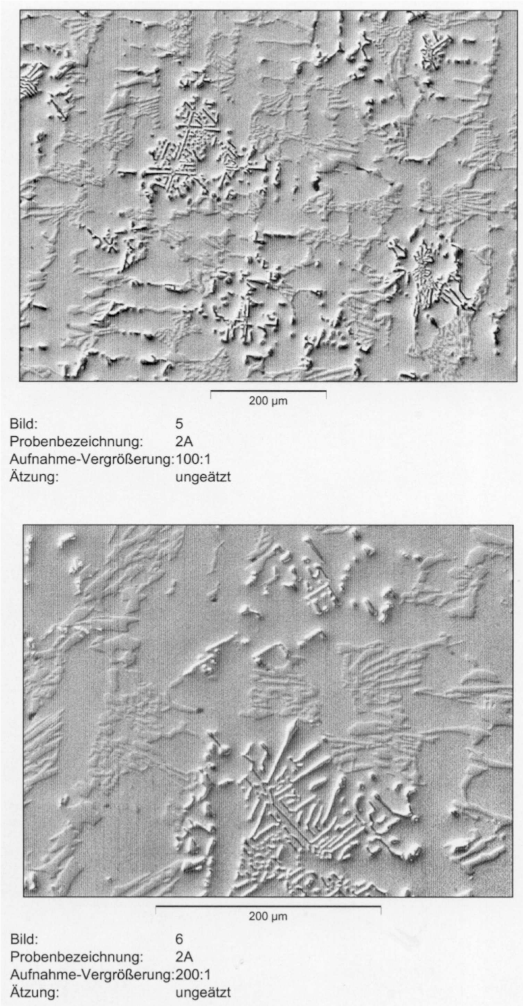

Figure 8. Microstructure of the cast alloy 2A (2.3 % C; 19.2 % Cr; 2.0 % Nb). Etched 5 % Nital and relief polished with alumina.

In the alloy with 2% V (alloy 1A in Table 1) the chromium carbides were harder. An average value of 1673 HV was found. In the alloy with 4% vanadium (1B) the average hardness value increased to 1960 HV. That means

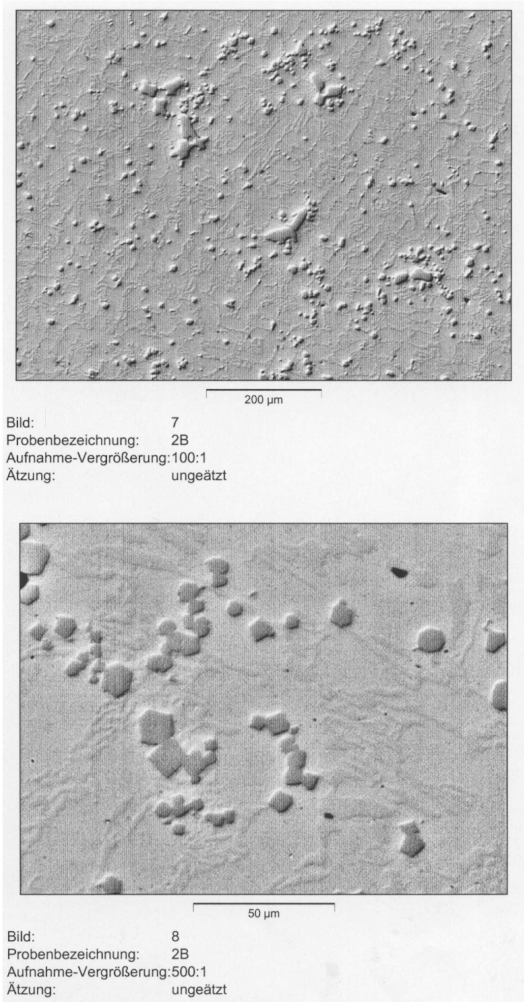

Figure 9. Microstructure of the cast alloy 2B (2.9% C; 19.2% Cr; 4.0% Nb). Etched 5% Nital and relief polished with alumina.

the hardness of the chromium carbide Cr_7C_3 increases by about 115 HV per added percent vanadium by solid solution hardening as Fig. 10 demonstrates.

In the niobium alloyed test melts 2A and 2B (Table 1) the hardness of the carbides could surely be measured only in the alloy with 4% niobium. The

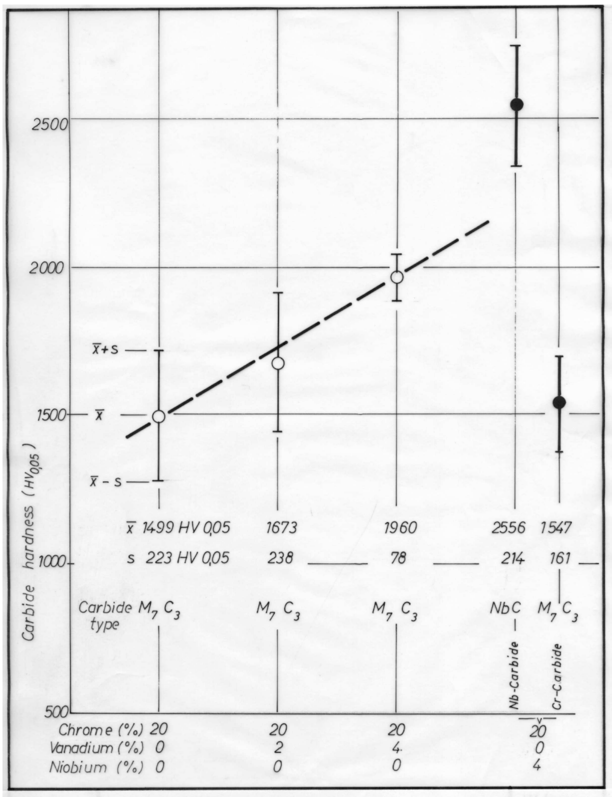

Figure 10. Carbide types and carbide hardness in high chromium alloyed tool steels with additions of vanadium or niobium.

cubic shaped niobium carbides showed a very high average hardness value of 2556 HV as it is known of pure NbC (see Fig. 1). Contrary to the above, the chromium carbides in the eutecticum showed only an average hardness of 1547 HV. That means that the chromium carbide is scarcely alloyed with niobium. The total of the niobium in the melts must have been completely bound in the niobium carbide.

The hardness tests confirm the results of the microstructure examination. In high chromium alloyed tool steels vanadium does not form a particular carbide. The added vanadium is dissolved in chromium carbide and increases the hardness of the Cr_7C_3 carbides by solid solution hardening. On the other hand, niobium forms a very hard particular niobium carbide in chromium alloyed tool steels already at low niobium contents (see Fig. 10).

SCALING AT HEAT TREATMENT OF CHROMIUM ALLOYED TOOL STEELS WITH ADDITION OF VANADIUM OR NIOBIUM

Chromium alloyed tool steels as a rule show a normal scaling behaviour. That means that the oxide skin protects the surface against the attack of oxygen and the growth of the oxide coating decreases with heat treating time. But when vanadium is added to high chromium alloyed tool steels, there are alloys that show an unusual growth of the oxide coating. Alloys that tend to such excessive growth of the oxide coating can be destroyed after a short annealing time as Fig. 11demonstrates. Such excessive oxidation has not been noticed with niobium alloyed chrome steel.

The sensibility of an alloy to excessive oxidation can be noticed by annealing a steel cube. If the alloy oxidate catastrophically, the oxide layer of the cube grows vertically to the surface and the edges of the cube burst as Fig. 11 shows. The temperature at which catastrophic oxidation occurs depends on the steel type. The influence of the annealing temperature can be remarkable. E.g. with an alloy of 20% Cr and 4% V no unusual oxidation is to be noticed at 770 ℃annealing temperature. Already after an increase of the temperature of 30 ℃the catastrophic oxidation starts and the cube is completely oxidised at 830 ℃after some hours (Fig. 11).

In the oxide coating one can find oxides of all alloying elements of the steels under consideration. In all steels with catastrophic oxidation V_2O_5 is to be found in the coating. But there are also alloys that have V_2O_5 in the coating and show a normal oxidation. Probably the catastrophic oxidation is influenced by the solution of vanadium in chromium carbide. High vanadium alloyed steels do not tend to unusual oxidation when vanadium is less dissolved in chrome carbide and when Vanadium forms a particular carbide VC.

The mechanism that influences the oxidation behaviour has not been further investigated. But it has been tried by many oxidation tests to find the border between alloy areas that oxidise normally and those which show the catastrophic oxidation (Table 3). Figures 12, 13, 14 show some examples of the tests.

Table 3. Commercial steels used for oxidation tests

Commercial name or steel grade	Average Chemical Composition [wt%]							
	C	Si	Mn	Cr	Mo	W	V	Co
W.-Nr. 3355 (T1)	0,80	0,40	0,30	4,20	0,70	18,00	1,50	4,80
Vanadis 23 (M3)	1,28			4,20	5,00	6,40	3,10	
S 690 (M4)	1,33			4,30	4,90	5,90	4,10	
S 390 (T15)	1,60			4,80	2,00	10,50	5,00	8,00
CPM 10V	2,45			5,25	1,30		9,75	
W.-Nr. 2344 (H13)	0,40	1,10	0,40	5,20	1,40		1,00	
Vanadis 4	1,50	1,00	0,40	8,00	1,50		4,00	
Vanadis 10	2,90	1,00	0,50	8,00	1,50		9,80	
M 390	1,90	0,70	0,30	20,00	1,00		4,00	
Chipper	0,50	1,00	0,50	8,00	1,50		0,50	
W.-Nr. 2379 (D2)	1,55	0,30	0,40	11,80	0,80		0,95	
K 190	2,30	0,40	0,40	12,50	1,10		4,00	
Elmax	1,70	0,80	0,30	18,00	1,00		3,00	
CPM T440V	2,15			17,50	0,50		5,75	
W.-Nr. 4528	1,05	0,80	0,80	17,50	1,30		0,10	1,50
W.-Nr. 4741	0,10	2,20	0,80	18,00				

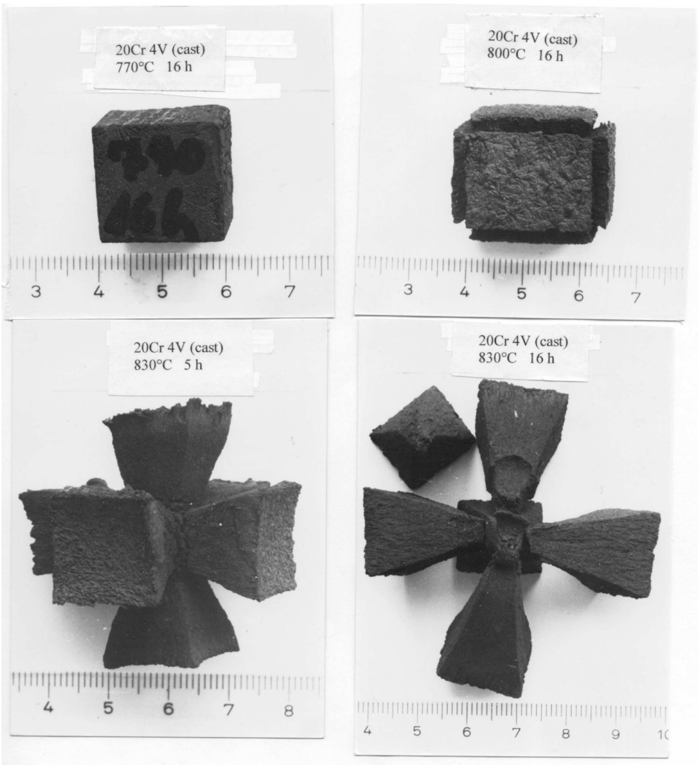

Figure 11. Catastrophic oxidation of a 20 mm cube at an alloy with 20% Cr and 4% V.

The result of the oxidation tests is demonstrated in Fig. 15. In steels with higher chromium contents small amounts of vanadium are sufficient to cause catastrophic oxidation. For steels with chromium contents of less than 8% the probability of unusual oxidation is small.

According to our tests, the kind of oxidation only depends on the chemical analysis of the steel and not on the manufacturing process. Cast alloys and PM-steels show the same behaviour. The higher oxidation rate of cast material is only due to the porosity of the cast state.

The danger of unusual oxidation virtually exists only when heat treatment is done on air with an unprotected surface. During the manufacturing process, PM steels sensitive to oxidation are protected by the casing. The

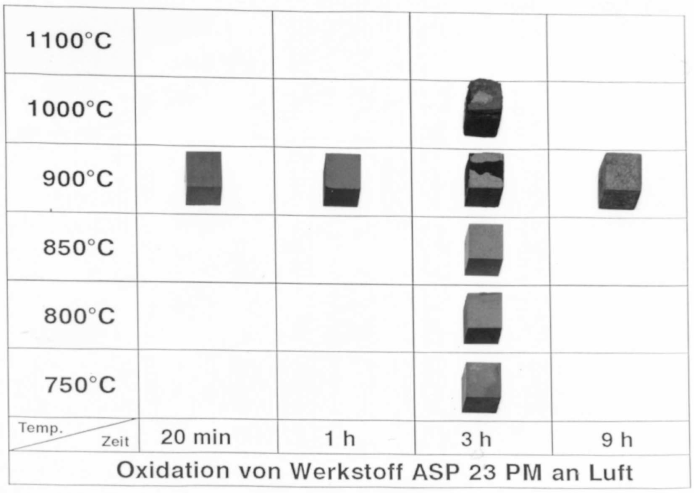

Figure 12. Oxidation of cubes of Vanadis 23.

heat treatment of tools also causes no difficulties when it is done in vacuum furnaces or in protected atmosphere.

WEAR RESISTANCE OF CHROMIUM ALLOYED TOOL STEEL WITH ADDITIONS OF VANADIUM OR NIOBIUM

Only some comparison tests were carried out with cast alloys of Table 1 containing 2 and 4% vanadium or niobium. In the tests (Amsler method) two rolls of 36 mm ∅ were pressed together with a power of 100 N. The test material roll was driven with 180 rpm and the reference roll made of CPM 10 V with 160 rpm. By the slip that exists between the two rolls a galling wear is caused. The test material was hardened to 63 HRC while the reference roll made of CPM 10V had a hardness of 64 HRC.

After a given test time, following material abrasion resulted of the galling test, see table 4.

The test material 2B with the large amount of very hard cubic carbides in the microstructure has regularly levigated the material of the reference roll. Though the material with 4% Nb showed big advantages in wear resistance, it has not been used for cylinders in plastic machines. One feared this cylinder

Table 4. Results of wear test

Type of test material	Material loss	Loss of the reference roll
Nr. 1A: 19.5% Cr 1.9% V	650 mg	124 mg
Nr. 1B: 19.5% Cr 4.0% V	320 mg	124 mg
Nr. 2A: 19.2% Cr 2.0% Nb	200 mg	33 mg
Nr. 2B: 19.2% Cr 4.0% Nb	– 14 g (weight increase)	280 mg

material would attack the extruder worm too much and would shorten the tool life of the worm too much.

CONCLUSION

The carbide forming elements vanadium and niobium show the following influences in high chrome alloyed tool steels.

At the manufacturing of melts and at gas atomizing the addition of vanadium up to percentages of 10% causes no difficulties. On the other hand, the alloying of niobium is limited to about 4%. Niobium carbide directly precipitates in the melt and makes the melt viscous and unsuitable for gas atomizing at higher niobium contents.

At hardening temperature the solubility of niobium in austenite is insignificantly small. Therefore – contrarily to vanadium – the contribution of niobium to secondary hardness is insignificant. But because of the small solubility, NbC is suitable to control the austenite grain size on hardening temperature.

Vanadium does not form separate vanadium carbides of the type MC in high chromium alloyed tool steel. The total amount of vanadium is dissolved in the chromium carbide Cr_7C_3 , whose hardness increases by about 115 HV per added percent vanadium. On the other hand already small amounts of niobium additions lead to the formation of the very hard niobium carbide. NbC is directly formed in the melt as a cubic crystal if the niobium amount in the alloy exceeds 2.5%. At lower contents the niobium carbides show a more eutectic form in the microstructure.

Vanadium and niobium have different influences on the carbide hardness. In high chromium alloyed tool steels the vanadium content is completely solved in the chromium carbide Cr_7C_3 and increases the hardness by solid solution hardening by about 115 HV per percent vanadium added. In niobium alloyed chromium tool steels always two carbide types are to be found, namely the niobium free Cr_7C_3 with about 1500 HV hardness and the very hard cubic crystallized NbC with about 2500 HV.

Big differences between vanadium and niobium in chromium alloyed tool steels are to be noticed at scaling during heat treatment. Niobium alloyed tool steels show the normal oxidation behaviour like the niobium and vanadium free chromium alloyed tool steels. With the addition of vanadium to high chromium alloyed tool steel, a catastrophic scaling is possible, if the chromium content is higher that 8%. The unusual scaling only depends on the analysis and not on the manufacturing process of the steel.

Some wear tests indicate that Nb-alloyed steels are superior to vanadium alloyed steels, if their microstructure has higher amounts of cubic NbC that have been precipitated in the melt.

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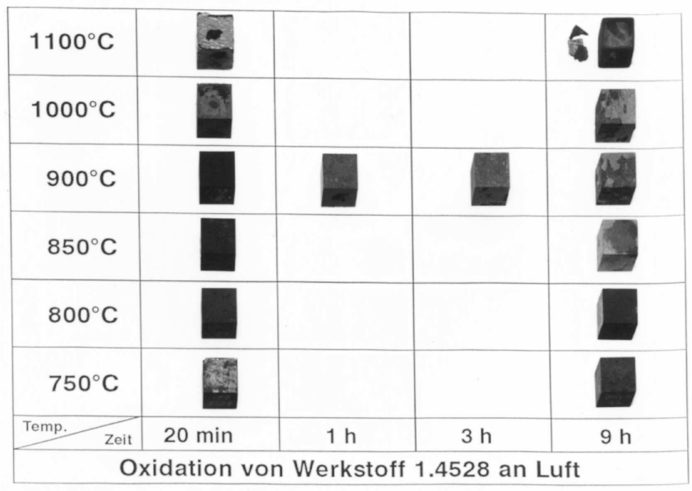

Figure 13. Oxidation of the Chromium alloyed tool steel 1.4528.

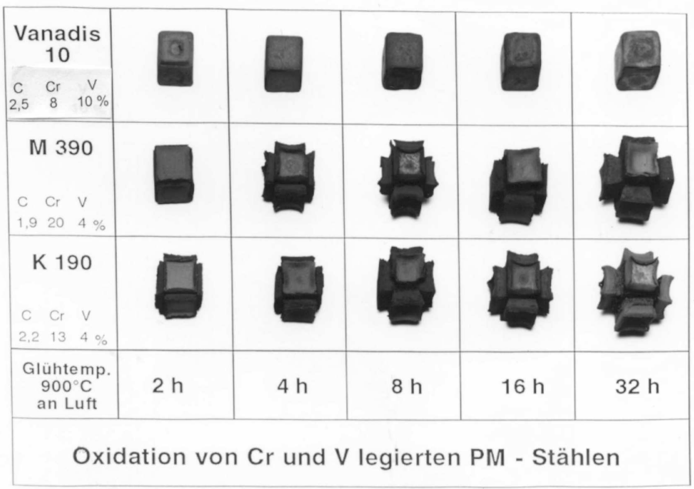

Figure 14. Oxidation behaviour of Vanadis 10, M390 and K190.

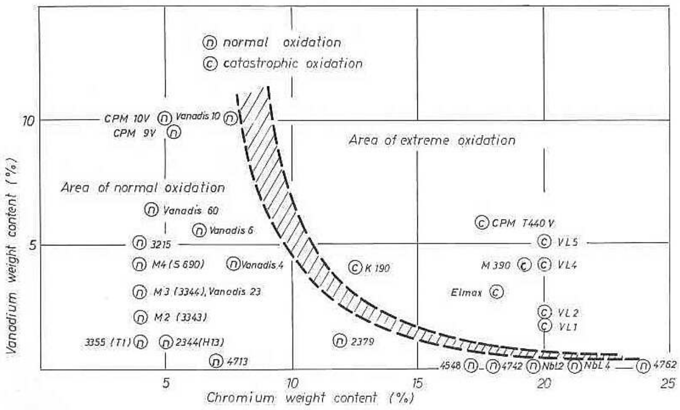

Figure 15. Area with catastrophic scale formation in steels with high chromium and vanadium contents.