CARBIDE DISSOLUTION RATE AND CARBIDE CONTENTS IN USUAL HIGH ALLOYED TOOL STEELS AT AUSTENITIZING TEMPERATURES BETWEEN 900 ℃ AND 1250 ℃.

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Abstract The wear resistance of cold work steels essentially depends on the amount and on the types of undissolved carbides present in the hardened condition. The aim of this paper is to show the differences of carbide content in tool steels for cold work used today. Only the content of undissolved carbides after heat treatment is important for wear resistance. Therefore the changes of carbide content by heat treatment have been determined. The rate of carbide solution at austenitizing temperature and the time to reach equilibrium structure were also tested.

Keywords: Wear, high alloyed tool steels, carbides

INTRODUCTION

At a given hardness the abrasive wear resistance of cold work steels depends on the amount, size and distribution of undissolved primary carbides and of the carbide types after austenitizing [1, 2, 3, 4, 5]. Beyond this, the wear resistance can be influenced by the size [4, 5, 6, 7] and the spacing [5, 7, 8, 9] of the carbides. If size and spacing of the carbides are very similar as for example in PM tool steels [6], their wear resistance at a defined hardness depends only on the amount and the type of undissolved carbides.

For this present investigation it has been tested which amount of carbides and which types of carbide are to be found in nine customary used PM tool

steels and in a conventionally produced tool steel (AISI D2) after austenitizing at 900 °C to 1250 °C. The results make it possible to compare the steel grades with regard to their expected wear resistance and to classify them at growing wear resistance. Of interest is also to which extend the amount of undissolved carbides is changed by the hardening temperature. The carbide content must be evaluated in the equilibrium state. Therefore the dissolution rate of carbides had to be determined.

The amount of present carbides has been measured by electrochemical carbide extraction [10, 11, 12], and the identification of the nature of the carbides has been made by X-ray structure analysis.

TESTED STEEL TYPES AND THEIR HEAT TREATMENT

The tests have been performed on nine PM tool steels used today and for comparison on a conventionally produced tool steel W.-Nr. 1.2379 (AISI D2). Table 1 shows the tested steel types and their chemical compositions.

The steel specimens were heat treated in salt bath, because here the heating rate and the soaking time can be very well reproduced for a certain specimen size. The test pieces were hardened in a large temperature range from 900 °C to 1250 °C. Before austenitizing, the samples were preheated 10 min. in the starting salt bath of 800 °C. The holding time in the salt bath at austenitizing temperature was 5 min. for bath temperatures higher than 1150 °C and 20 min. in salt bathes at lower temperatures. After austenitizing, the samples were quenched in a salt bath of 560 °C and after 5 min. further cooled in air.

DETERMINATION OF THE AMOUNT OF UNDISSOLVED CARBIDES AND IDENTIFICATION OF THEIR NATURE

The extraction of undissolved carbides after austenitizing was carried out electrochemically. In an electrolyte of 5 % muriatic acid and 95 % methyl alcohol the matrix of the samples is dissoluted with an intensity of current of 5 mA/cm². The dissolution potential of the matrix is about 500 mV and much lower than that of the carbides with about 900 mV. Therefore it is possible to dissolve the matrix completely without attacking the carbides. The electrolytic dissolution of the matrix was done galvanostatically, because

under these conditions a quantitative extraction of carbides can be expected [10, **?**, 12].

The extracted amount of carbides can include small parts of the carbon dissolved in the matrix in colloidal solution [11]. Thereby the measured amount of extracted carbides is a little too high. The fault in weight content is however less than 2 % of the mass of the extracted carbides. Therefore the fault was not taken into account at the weight of undissolved carbides.

Whereas the total amount of carbides was measured on all tested samples, the nature of the extracted carbides was only tested in the annealed condition and after austenitizing at 1150 ℃ or 1200 ℃. The carbide identification was made by X-ray structural analysis and by use of the ASTM card index.

RATE OF CARBIDE DISSOLUTION AT AUSTENITIZING TEMPERATURE AND TIME TO ACHIEVE EQUILIBRIUM IN THE MICROSTRUCTURE

A comparison of the carbide content of the investigated steels is only possible if the microstructure is in equilibrium. At that state the content of carbides is at a minimum. Because of the lack of reliable information, instructions and technical booklets [13], first the heat treatment conditions to achieve equilibrium were examined. The temperature in the samples was measured by thermocouples in bore holes of 1 mm ∅ during heating in salt bath. Figures 1 and 2 show examples of the tests. Figure 1 shows the temperature in the core of HSS-specimens of 5 to 50 mm ∅ during heating from 850 ℃ to 1250 ℃. The samples were immersed from 850 ℃ in a bath of 1250 ℃. Figure 2 shows the temperature distribution in samples of 20 and 50 mm ∅ during heating from 1050 ℃ to 1250 ℃. The bore for the edge temperature had a distance of 0.5 mm from the sample surface. Comparing the temperature gradient in different heating temperature areas one can see that a given sample size needs always nearly the same soaking time independent from the temperature range covered.

Thus for a sample size of 20 mm ∅ the soaking time in a salt bath is 90 s, for the heating step 850–1250 ℃ as well as for the heating step 1050–1250 ℃. Theoretically the edge reaches the bath temperature at the same time as the core. For practical use the surface temperature is achieved earlier, for 20 mm ∅ samples after about 70 s and for 10 mm ∅ samples after 30 s.

As the soaking time is very short for the specimens used, it was not taken into consideration at the measurements of carbide dissolution times.

The determination of the time to achieve equilibrium in the microstructure was carried out with high speed steel samples of 10 mm ∅ and 50 mm length. As there is a common idea that structures with coarse primary carbides have a lower solution rate than those with smaller carbides, the equilibrium tests were done with steel billets of different microstructure. The used steel billets had primary carbide sizes of about 1 µm, of 3–5 µm and of 10–15 µm. Figure 3 shows the microstructures.

The different carbide sizes were manufactured by annealing billets at different temperatures before rolling as it has been described in literature [7, 14]. The rate of carbide dissolution was examined at temperatures from 1170 to 1250 °C in salt bath. The immersion times were 30 s, 1 min, 2 min, 4 min, 8 min, 16 min and 32 min after preheating them at 800 °C in salt bath.

Figures 4 and 5 show the influences of temperature and time on the carbide solution. As one can see, the dissolution rate is very high. Already in the first 30 s of immersion which are necessary to reach the bath temperature at the sample surface, nearly 80% of the maximum soluble amount of carbides have been dissolved. Furthermore the figures indicate that equilibrium is reached within 5 min for all austenitizing temperatures above 1150 °C.

At lower bath temperatures the adjustment of the equilibrium needs some more time. For instance the PM tool steel K190 that has in the annealed condition 25.6 weight % carbides has at 1000 °C after 5 min immersion time still 23.5 % carbides, after 10 min 23.2 %, after 15 min 22.9 %, and after 20 min 23.0 weight % carbides were measured. That means that equilibrium has adjusted at 1000 °C between 10 and 15 min.

Interesting and remarkable is the influence of the size of the primary carbides on the dissolution rate. At all tested temperatures the dissolution rate in structures with coarse carbides is clearly higher than with smaller carbides. The following explanation can be offered. To manufacture a structure with coarse carbides, the billets have to be heated at higher temperatures before rolling. Thereby in these billets more carbides are dissolved than in billets which are heated at lower temperature. The amount of dissolved alloying elements does not diffuse back during rolling and the following heat treatment. They remain in the matrix and precipitate in form of very small carbides in the matrix. Due to the higher amount of very small carbides distributed in the matrix, the matrix is here faster saturated with alloying elements at

hardening temperatures. Therefore steels with coarse primary carbides are easier to harden than those with a fine carbide structure. But this is only true, if the coarse carbides have been formed by coagulation at high temperature. If coarse carbides result from other reasons, e.g. by means of solidification as in HSS type AISI T18, one can not necessarily expect a quick carbide dissolution at austenitizing.

COMPARISON OF THE QUANTITY OF UNDISSOLVED CARBIDES IN STANDARD TOOL STEELS USED TODAY

The comparison tests have been made with the steel grades of Table 1. The samples for the electrochemical carbide extraction had a size of 20 mm ∅ and 15 mm length. The samples were austenitized in the range from 900 ℃ to 1250 ℃. According to the results of the equilibrium tests, the immersion times were 5 min for temperatures above 1150 ℃ and 20 min for lower temperatures.

Table 1. Tested Steel Grades and their Chemical Composition

Steel grade EN ISO 4957	AISI-№.	Commercial Name	Chemical Composition (average values, %)							
			C	Si	Mn	Cr	Mo	W	V	Co
HS6-5-3	M 3:2	Vanadis 23	1,28	–	–	4,2	5,0	6,4	3,1	–
HS6-5-3-9	M 3:2 +Co	Vanadis 30	1,28	–	–	4,2	5,0	6,4	3,1	8,5
HS7-7-7-10	—	Vanadis 60	2,30	–	–	4,2	7,0	6,5	6,5	10,5
X150 CrVMo 8-4	—	Vanadis 4	1,50	1,0	0,4	8,0	1,5	–	4,0	–
X290 VCrMo10-8	—	Vanadis 10	2,90	1,0	0,5	8,0	1,5	–	9.8	–
X230 CrVMo 12-4	—	Böhler K190 PM	2,30	0,4	0,4	12,5	1,1	–	4,0	–
HS10-2-5-8	≃ T15	Böhler S390 PM	1,60	–	–	4,8	2,0	10,5	5,0	8,0
HS6-5-4	M4	Böhler S690 PM	1,33	–	–	4,3	4,9	5,9	4,1	–
X190 CrVMo 20-4	—	Böhler M390 PM	1,90	0,7	0,3	20,0	1,0	0,6	4,0	–
X153 CrMoV 12	D2	Sverker 21	1,55	0,3	0,4	11,8	0,8	–	0,8	–

In Fig. 6, the results of the carbide determination are shown.

In the annealed condition the tested steel grades have carbide amounts between 15 and 30 weight %. In all tested tool steels the amount of undissolved carbides clearly decreases when the austenitizing temperature increases. The decrease of the amount of undissolved carbides mostly drops linear with increasing hardening temperatures. As is to be seen, the content of carbides is reduced by approximately 35 to 45 % when the annealed state is heated to 1200 ℃.

Table 2: Amount of undissolved carbides and carbide types after heat treatment

Steel grade EN ISO 4957	Commercial Name	Heat treatment	Amount of undissolved carbides (%)	Types of carbides and their weight percentage (%)
HS6-5-3	Vanadis 23	Annealed	23,5	V_8C_7; Mo_2C; $(Fe_3W_3)C$ – $(Fe_4W_2)C$
HS6-5-3	Vanadis 23	1200 ℃/5’	14,4	25,4 % V_8C_7; 48,3 % V_4C_3; 26,3 % $(Fe_3W_3)C$-$(Fe_4W_2)C$
HS6-5-3-9	Vanadis 30	Annealed	22,2	Cr_7C_3; V_8C_7; V_4C_3; $(Fe_3W_3)C$-$(Fe_4W_2)C$
HS6-5-3-9	Vanadis 30	1200 ℃/5’	15,7	V_8C_7; V_4C_3; $(Fe_3W_3)C$-$(Fe_4W_2)C$
HS7-7-7-10	Vanadis 60	Annealed	29,6	Cr_7C_3; V_8C_7; V_4C_3; Mo_2C; $(Fe_3W_3)C$-$(Fe_4W_2)C$
HS7-7-7-10	Vanadis 60	1200 ℃/5’	24,8	V_8C_7; V_4C_3; $(Fe_3W_3)C$-$(Fe_4W_2)C$
X150 CrVMo 8-4	Vanadis 4	Annealed	14,8	64,3 % Cr_7C_3; 35 % V_8C_7
X150 CrVMo 8-4	Vanadis 4	1150 ℃/15’	9,1	34,3 % Cr_7C_3; 12,5 % V_4C_3; 53,4 % V_8C_7
X290 VCrMo10-8	Vanadis 10	Annealed	23,7	37,1 % Cr_7C_3; 9,5 % V_4C_3; 53,4 % V_8C_7
X290 VCrMo10-8	Vanadis 10	1200 ℃/5’	19,7	17,3 % Cr_7C_3; 5,8 % V_4C_3; 76,6 % V_8C_7
X230 CrVMo 12-4	Böhler K190 PM	Annealed	25,6	84,1 % Cr_7C_3; 15,9 % V_4C_3
X230 CrVMo 12-4	Böhler K190 PM	1150 ℃/5’	21,7	81,0 % Cr_7C_3; 16,9 % V_4C_3
HS10-2-5-8	Böhler S390 PM	Annealed	25,4	Cr_7C_3; V_8C_7; $(Fe_3W_3)C$-$(Fe_4W_2)C$
HS10-2-5-8	Böhler S390 PM	1200 ℃/5’	19,0	59 % V_8C_7; 41 % $(Fe_3W_3)C$-$(Fe_4W_2)C$
HS6-5-4	Böhler S690 PM	Annealed	21,9	Cr_7C_3; V_8C_7; $(Fe_3W_3)C$-$(Fe_4W_2)C$
HS6-5-4	Böhler S690 PM	1200 ℃/5’	12,6	V_8C_7; $(Fe_3W_3)C$- $(Fe_4W_2)C$
X190 CrVMo 20-4	Böhler M390 PM	Annealed	28,6	91 % $(Cr)_{23}C_6$; 9 % V_4C_3
X190 CrVMo 20-4	Böhler M390 PM	1200 ℃/5’	17,6	$(Cr)_7C_3$; V_4C_3 (small amount)
X153 CrMoV 12	Sverker 21	Annealed	18,0	83,5 % Cr_7C_3; 16,5 % $(Cr,Fe)_7C_3$
X153 CrMoV 12	Sverker 21	1150 ℃/15’	11,0	90 % Cr_7C_3; 9,4 % $(Cr,Fe)_7C_3$

When the amount of carbides drops, normally the wear resistance should also decrease. But one also has to take into account the type of carbide, that means the hardness of carbides. Table 2 gives some information of the carbide types to be found in the annealed and in the at 1150 $^{\circ}C$ or 1200 $^{\circ}C$ hardened condition. Table 2 also shows how the types of carbides and the weight percentage of the carbide types are changed by the heat treatment. The weight percentage of the stable carbide type MC increases whilst the content of the less stable carbide types $M_{23}C_6$ or M_7C_3 is reduced, changed to more stable carbide types or are completely dissolved. If one takes into consideration not only the amount but also the types of carbides, it explains why the tool steel Vanadis 4 has a higher wear resistance than the more carbide rich ledeburitic tool steel Sverker 21 (AISI D2). In Vanadis 4 after austenitizing, two thirds of the undissolved carbides are of the type VC that has a very high hardness of 2500 HV. On the other hand the hardened Sverker 21 only has chromium carbides of the type M_7C_3 with about 1200 HV hardness.

Also of interest is the comparison of the carbide content curves of the steel Vanadis 23 and Vanadis 30. Both steels only distinguish themselves by an alloying addition of 9 % cobalt. As the content of carbide forming alloying elements is the same, in Fig 6 the curves of both steels lie in a small scatterband. That means for cold work purposes that the higher alloyed Vanadis 30 brings no advantage in tool life at cold working use.

Fig 6 indicates some more information of practical interest. When one can reach a specified hardness at 1000 $^{\circ}C$ hardening temperature as well as at 1200 $^{\circ}C$, it is more advantageous to choose the lower temperature. At 1000 $^{\circ}C$ hardening temperature the microstructure has between 15 and 50 % more carbides, which can reduce wear resistance. The gain of weight percentage of carbide content is higher for lower alloyed steels like Vanadis 4 and lower for very high alloyed steels, i.e. Vanadis 10.

According to this investigation lower hardening temperatures do not only lead to higher toughness of tool steel [14, 15], but also to more carbides in the structure that can increase the wear resistance.

SUMMARY

After this investigation the dissolution rate of carbides in high alloyed tool steel is unexpectedly high. Already after 30 s immersion time in a salt bath, 80 % of the possible amount of dissoluble carbides are in solution. The solution equilibrium is reached after 5 min for temperatures above 1150 $^{\circ}C$.

At lower hardening temperatures, about 10 min are necessary to achieve maximum carbide solution. Surprising is that in structures with big primary carbides that have been coarsed at higher temperatures, the rate of dissolution is not slower but clearly faster than in a steel state with small primary carbides.

The high alloyed tool steels used today have total weight percentages between 15 and 30 % in the annealed condition. For the evaluation of the influence on wear resistance not only the amount of carbides but also the types of carbides are of importance. Otherwise one draws the wrong conclusions as the comparison of the 4 % Vanadium tool steel Vanadis 4 and the conventionally manufactured tool steel Sverker 21 (AISI D2) shows.

By application of higher hardening temperatures, the carbide content decreases rather rapidly. At 1200 ℃hardening temperature, 35 to 45 % of the carbides present in the annealed state are dissolved. To make carbides useful to improve wear resistance, lower hardening temperatures should be chosen. At 1000 ℃hardening temperature, the amount of undissolved carbides is 15 to 50 % larger than at 1200 ℃. Low hardening temperatures do not only bring about more toughness in a tool, as it has been known for a long time, but also lead to a higher amount of undissolved carbides that can improve the wear resistance of cold work steels.

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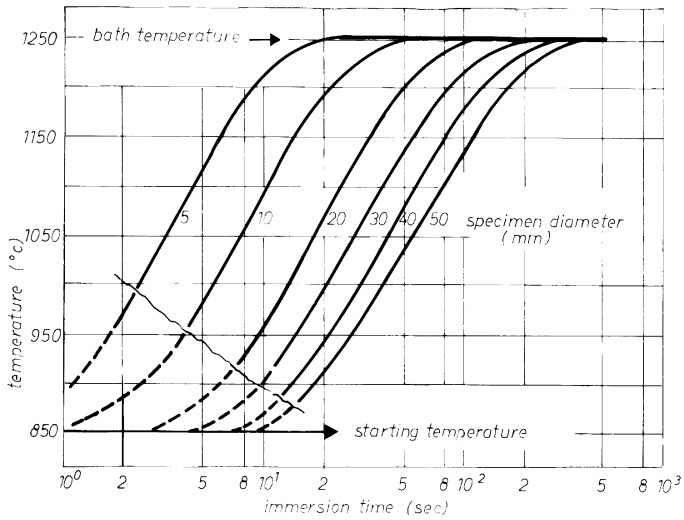

Figure 1. Temperature in the core of HSS-specimens (M2) during heating from 850 to 1250 °C in a salt bath.

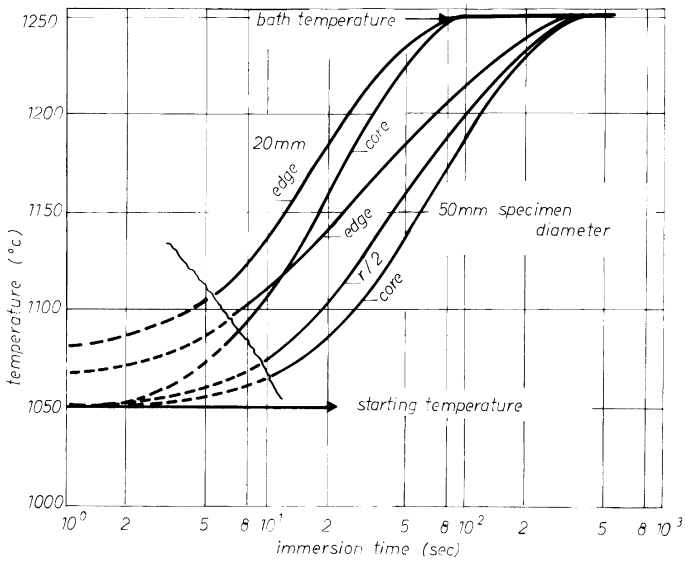

Figure 2. Temperature distribution between edge and core of HSS-specimens (M2) during heating from 1050 to 1250 °C in a salt bath.

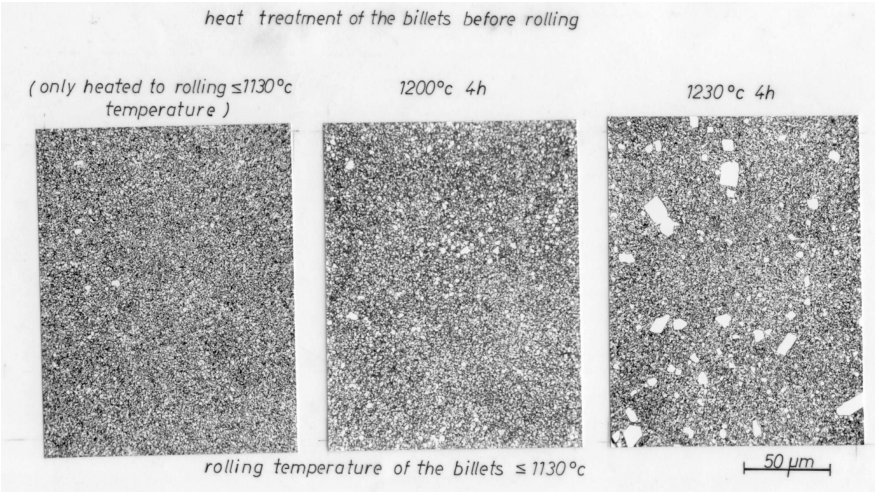

Figure 3. Coarsening of carbides in high speed steel HS2-9-1 (M1) by heat treatment of the billet before rolling.

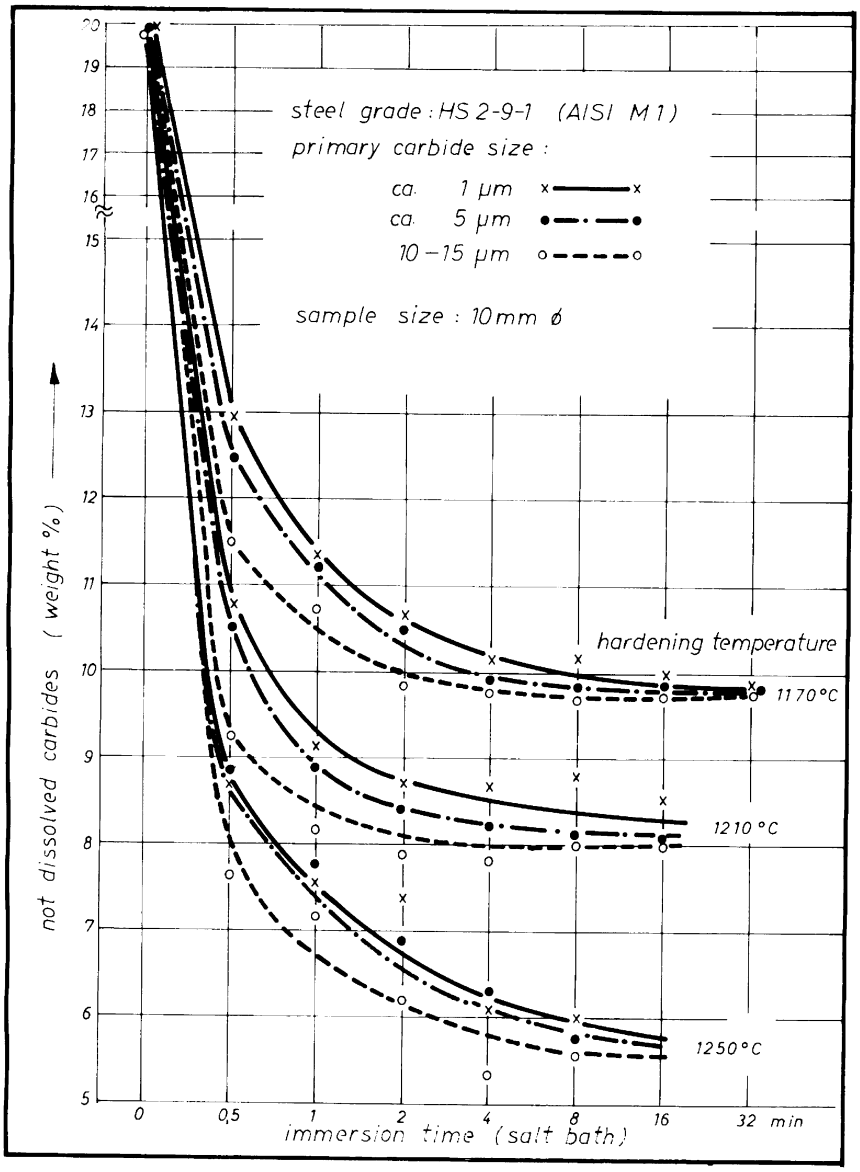

Figure 4. Solution rate of carbides at different immersion times in a salt bath of 1170 °C, 1210 °C and 1250 °C and the influence of primary carbide size.

Figure 5. Solution rate of carbides at different immersion times in a salt bath of 1190 °C and 1230 °C and the influence of primary carbide size.

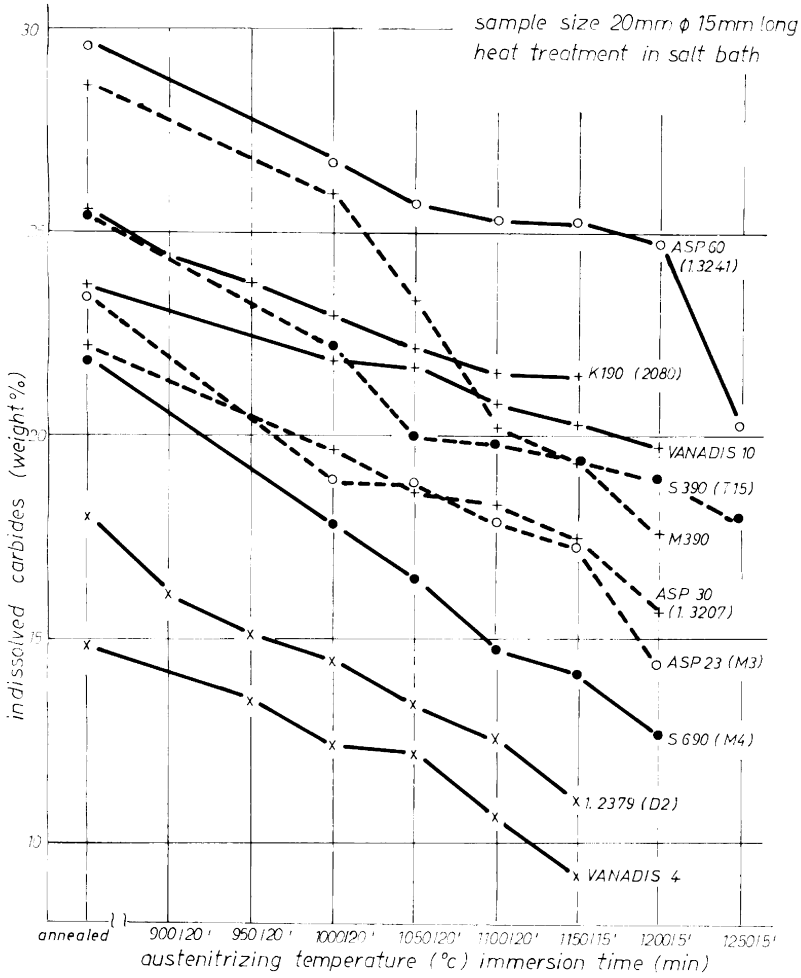

Figure 6. Amount of undissolved carbides in PM tool steels compared to the conventionally produced tool steel type D2 in the annealed and austenitized condition.