Bele kromove litine za valje, legirane z molibdenom

White Chromium Cast Irons for Rolls, Alloyed with Molybdenum

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Kromove bele litine, legirane z molibdenom in še ne-katerimi drugimi elementi, se zaradi dobre obrabne obstojnosti, trdote in zadovoljivih mehanskih lastnosti vedno več uporabljajo za dvoslojno lite valje. Litine imajo tudi dobro korozijsko obstojnost.

Delo obravnava mikrostrukturne značilnosti zlitin v litem stanju in po toplotni obdelavi. Narejena sta izotermna transformacijska diagrama za destabilizacijo avstenita in destabiliziran avstenit in kontinuirni transformacijski diagram za destabiliziran avstenit.
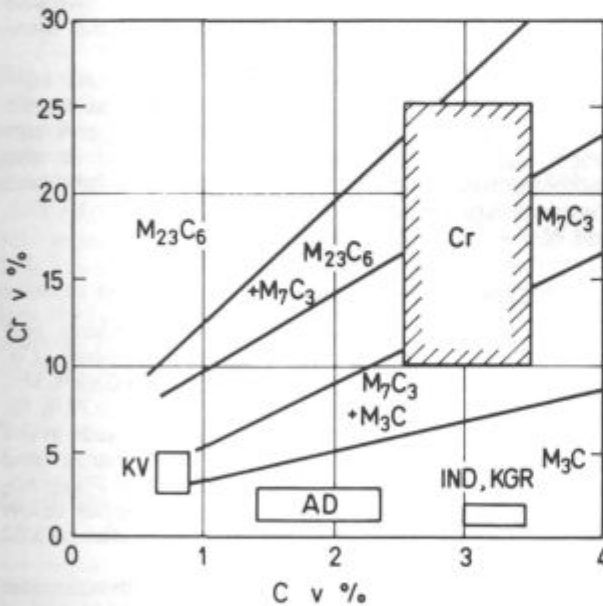
Chromium white cast irons alloyed with molybdenum and some other elements are more and more applied for compound cast rolls due to good wear resistance, hardness, and satisfactory mechanical properties. The cast irons have also good corrosion properties.

Paper treats the microstructural characteristics of cast irons as cast, and after the heat treatment. Isothermal transformation diagrams for the destabilization of austenite, and for the destabilized austenite were constructed next to the continuous transformation diagram for the destabilized austenite.

UVOD

V valjarnah je poleg ustrezne kvalitete valjanih proizvodov zelo pomembna ekonomičnost proizvodnje. Določena jekla se vroče valjajo v nizkih temperaturnih

INTRODUCTION

In rolling plants, the economy of manufacturing is very important next to the suitable quality of rolled products. Some steel is hot rolled in low-temperature regions with high partial reductions, and low permissible dimensional tolerances. Narower and narower tolerances are demanded also for the cold rolled strips. These are the reasons that rolls of white cast iron with high chromium content, and alloyed with Mo, Ni (Cu), V, Ti, and W are more and more used in hot and cold rolling plants. The rolls are cast by a compound centrifugal casting.

Data on chemical composition of rolls of white chromium cast irons are in references given in wide intervals. Data on manufacturing rolls, and on their heat treatment are scarce. The phase diagram in **Fig. 1** pres-
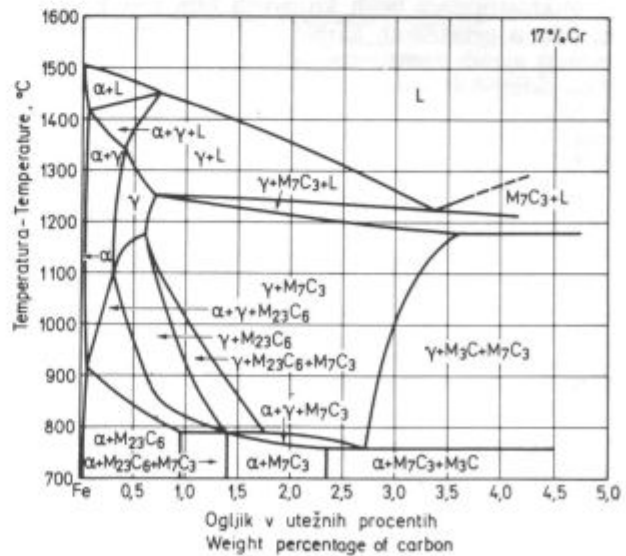

Sl. 1:
Kemična sestava belih kromovih litin in litin za druge vrste valjev v faznem diagramu (KV — kovani valji, AD — adamitni valji, IND — indefinitni valji, KGR — nodularni valji, Cr — bele kromove litine, 8)

Fig. 1
Chemical composition of white chromium cast irons, and cast irons for other types of rolls in the phase diagram (KV — forged rolls, AD — adamite rolls, IND — indefinite chill rolls, KGR — spheroidal-graphite rolls, Cr — white chromium cast irons, 8)
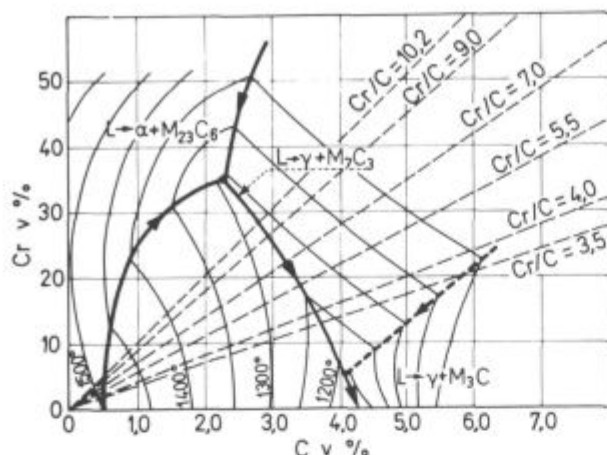

Sl. 2:
Fazni diagram Fe-Cr-C za 17 % Cr

Fig. 2
Fe-Cr-C phase diagram at 17 % Cr

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področjih z velikimi parcialnimi redukcijami, pri čemer se zahtevajo ozke dimenzijske tolerance. Vedno bolj ozke tolerance se zahtevajo tudi pri hladno valjanih trakovih. To so razlogi, da se v vročih in hladnih valjarnah vedno bolj uporabljajo valji iz bele litine z visoko vsebnostjo Cr, legirane še z Mo, Ni (Cu), V, Ti in W. Valji se izdelujejo po postopku dvoslojnega centrifugalnega litja.

Literaturni podatki o kemični sestavi valjev iz bele kromove litine so podani v širokih mejah. Podatki o izdelavi valjev in toplotni obdelavi so zelo skopi. V faznem diagramu na **sliki 1** je za primerjavo navedeno področje kemične sestave valjev iz bele kromove litine in drugih vrst valjev.

Zlitine Fe-Cr-C so že dolgo poznane in so v literaturi opisane številne raziskave. Fazni diagram Fe-Cr-C za 17 % Cr je prikazan na **sliki 2** (3). Za razvoj teh zlitin so poleg začetnih raziskav F. Osmonda, ki je v mikrostrukturi omenjenih litin že leta 1892 opazil kompleksne karbide, najpomembnejše raziskave R. S. Jacksona, ki je v faznem diagramu Fe-Cr-C opredelil likvidus površine **(sl. 3)** in sistematične raziskave vpliva Mo na mikrostrukturne značilnosti, ki sta jih naredila F. Maratray in R. Usseglio-Nanot (1, 2, 4).

Mikrostruktura belih kromovih litin sestoji iz primarnih in evtektičnih karbidov in avstenitne matice, oziroma njenih transformacijskih produktov (sekundarni karbidi, perlit, bainit, martenzit). Za mikrostrukturne značilnosti je zelo pomembno razmerje Cr/C in vsebnost legiranih elementov, predvsem Mo, Mn, Ni (Cu) in W.

EKSPERIMENTALNO DELO

Na osnovi literaturnih podatkov, ki smo jih imeli na voljo, smo v železarni Štore izdelali preizkusne taline z različno vsebnostjo legirnih elementov, in sicer z 2,5 do 3,8 % C, 11,3 do 19,4 % Cr, 0,39 do 0,66 % Mo, 0,59 do 1,37 % Si, 0,68 do 0,93 % Mn, 0,56 do 0,78 % Ni, 0,023 do 0,11 % Ti in z 0,06 do 0,11 % V. Štiri zlitine smo legirali z 0,80 do 0,93 % W. Zlitine legirane z W so trše in se uporabljajo za valje za hladno valjanje trakov. Vsebnost P mora biti pod 0,08 % in S pod 0,05 %. Preizkusne zlitine imajo razmerje Cr/C od 3,62 do 7,76.

Vzorce, preizkusne valjčke, premera 100 in višine 150 mm, smo ulili tako, da je bila polovica valjčka ulita v kokilo in polovica v pesek. Tako smo dobili na enem vzorcu dve različni hitrosti strjevanja.

Pogoji litja bistveno vplivajo na izoblikovanje mikrostrukture in s tem na mehanske lastnosti litine. Zato

ents the regions of chemical compositions of rolls of white chromium cast iron, and of some other types of rolls (8).

Fe-Cr-C alloys are already for a long time known, and numerous investigations are cited in references. The Fe-Cr-C phase diagram for 17 % Cr is shown in **Fig. 2** (3). For development of these alloys, the most essential are the investigations by R. S. Jackson who determined the liquidus surfaces in the Fe-Cr-C phase diagram **(Fig. 3)**, and the systematic investigations on the influence of Mo on the microstructural characteristics done by F. Maratray, and R. Usseglio — Nanot, beside the initial investigations by F. Osmond who already in 1892 observed complex carbides in the microstructure of the mentioned cast irons (1, 2, 4).

Microstructure of white chromium cast irons consists of primary and eutectic carbides, and austenitic matrix, or of its transformation products (secondary carbides, pearlite, bainite, martensite). Essential for the microstructural characteristics are the Cr/C ratio and the content of alloying elements, mainly Mo, Mn, Ni (Cu), and W.

EXPERIMENTAL WORK

Based on the data in references, being available, test melts with various contents of alloying elements, i. e. with 2.5 to 3.8 % C, 11.3 to 19.4 % Cr, 0.39 to 0.66 % Mo, 0.59 to 1.37 % Si, 0.68 to 0.93 % Mn, 0.56 to 0.78 % Ni, 0.023 to 0.11 % Ti, and 0.06 to 0.11 % V were made in the Štore Ironworks. Alloys with added W are harder and they are used for rolls for cold rolling of strips. Phosphorus content must be below 0.08 %, and sulphur below 0.05 %. The test melts had the Cr/C ratio between 3.62 and 7.76.

The samples as testing cylinders with diameter 100 mm and 150 mm high were cast so that one half of the cylinder was cast into mould, another one into sand. Thus two various solidification rates were obtained on the same specimen.

Casting conditions have essential influence on the formation of microstructure, and thus on the mechanical properties. Therefore melting points and solidification intervals were determined for some alloys.

Microstructural characteristics of as cast alloys, and after the heat treatment were determined by investigations with optical microscope, scanning electron microscope (SEM), and electron microanalyzer. To reveal the microstructural characteristics various etching agents (nital, Villela's, ferric chloride, alkaline picrate, Murakami's, and 4 % sodium hydroxide saturated with pota-

smo za nekatere zlitine določili temperature tališča in intervale strjevanja.

Mikrostrukturne značilnosti zlitin v litem stanju in po toplotni obdelavi smo opredelili s preiskavami z optičnim mikroskopom, v raster elektronskem mikroskopu (SEM) in v elektronskem mikroanalizatorju. Za odkrivanje mikrostrukturnih značilnosti smo uporabili različna jedkala (nital, Villela, feriklorid, alkalijski pikrat, Murakami in 4 % natrijev hidroksid, nasičen s kalijevim permanganatom). Sekundarne karbide in faze, nastale pri transformaciji avstenita, smo lahko dobro opredelili v SEM. V elektronskem mikroanalizatorju smo določili sestavo primarnih in evtektičnih karbidov in koncentracije nekaterih legirnih elementov v matici.

Za eno od zlitin z najustreznejšo kemično sestavo in mikrostrukturo smo naredili izotermna transformacijska diagrama za nedestabilizirano in destabilizirano avstenitno matico in kontinuirni transformacijski diagram za destabiliziran avstenit.

Od mehanskih lastnosti smo merili le trdoto zlitin in posameznih mikrostrukturnih faz. V literaturi smo zasledili raziskave, ki obravnavajo upogibno trdnost in žilavost teh zlitin (13). Za valje je poznavanje teh parametrov zelo pomembno, vendar smo zaradi težavne priprave mehanskih preizkušancev te preiskave odložili na kasnejši čas.

REZULTATI PREISKAV

Tališča in interval strjevanja zlitin

Žilavost in obrabna obstojnost litine je tem boljša, čim bolj drobni so evtektični karbidi in čim enakomerneje so porazdeljeni po matici. (19) Zato mora potekati strjevanje belih kromovih litin hitro. Pri previsokem pregretju in počasnem strjevanju lahko nastanejo poleg grobih evtektičnih klarbidov še veliki primarni karbidi.

V talilnem mikroskopu smo določili tališča in intervale taljenja nekaterih zlitin, izbranih tako, da smo pokrili ves interval razmerij Cr/C (tabela 1). Zaradi rekalescence je razlika med talilnim in strjevalnim intervalom majhna. Zlitine so močno izcejane in se rezultati paralelk in vrednosti, izmerjene večkrat na istem vzorcu, med seboj precej razlikujejo.

Tabela 1: Tališča in intervali taljenja

Zlitina	% C	% Cr	Cr/C	Nastanek kapljic °C	Začetek talj. °C	Staljeno °C	Interval talj. °C
1	2,49	19,31	7,76	1200	1245	1345	100
2	2,63	19,43	7,39	1170	1220	1350	130 (legirano z W)
3	2,72	14,90	5,48	1200	1250	1305	55
4	2,76	19,21	6,96	1210	1250	1325	75
5	3,20	17,95	5,61	1210	1250	1285	35
7	3,31	11,97	3,62	1190	1225	1300	75
8	3,48	16,23	4,66	1170	1215	1250	35 (legirano z W)

Zlitine imajo tališča med 1350 in 1250 °C. Čim bolj se sestava zlitine približuje evtektični sestavi, ožji je interval strjevanja. Na **sliki 2** se vidi, da ima zlitina s 17 % Cr evtektično sestavo pri 3,4 % C. Na tališče in in-

ssium permanganate) were applied. Secondary carbides, and phases formed during the transformation of austenite were well determined by SEM. Electron microanalyzer helped us to determine the composition of primary and eutectic carbides, and the concentrations of some alloying elements in the matrix.

For one of the alloys, with the most suitable chemical composition and the microstructure, the isothermal transformation diagrams for undestabilized and destabilized austenitic matrix, and the continuous transformation diagram for destabilized austenite were constructed.

Of mechanical properties only hardness of alloys and of single microstructural phases was measured. In references, investigations treating the bending strength, and the toughness of these alloys were found (13). Though the knowledge of these properties is very important for the behaviour of rolls, these investigations were postponed for later due to difficult preparation of testing specimens.

RESULTS OF INVESTIGATIONS

Melting Points and Solidification Interval of Alloys

Toughness and wear resistance of the alloy are the better the smaller are eutectic carbides, and the more uniformly they are distributed in the matrix (19). Therefore the solidification of white chromium cast irons must be fast. At a too high superheating and low solidification rate big primary carbides next to coarse eutectic carbides can be formed.

Melting points and solidification intervals of some alloys were determined by fusion microscope. The alloys were chosen in such a way that he whole interval of the Cr/C ratios was covered (**Table 1**). Due to recalescence the difference between the melting and the solidification interval is small. The alloys exhibit intensive segregating, thus the results of parallel tests, and the values measured more times on the same sample differ a great deal.

Table 1 Melting Points and Solidification Intervals

Alloy	% C	% Cr	Cr/C	Formation of drops °C	Begin. of melting °C	Melted °C	Melting interval °C
1	2,49	19,31	7,76	1200	1245	1345	100
2	2,63	19,43	7,39	1170	1220	1350	130 (alloyed with W)
3	2,72	14,90	5,48	1200	1250	1305	55
4	2,76	19,21	6,96	1210	1250	1325	75
5	3,20	17,95	5,61	1210	1250	1285	35
7	3,31	11,97	3,62	1190	1225	1300	75
8	3,48	16,23	4,66	1170	1215	1250	35 (alloyed with W)

The alloys have the melting points between 1350 and 1250° C. The closer is the alloy composition to the eutectic composition the narrower is the solidification interval. It is evident from the **Fig. 2** that the alloy with 17 % Cr has eutectic composition at 3.4 % C. The melting points and the solidification intervals are mainly influenced by the carbon content, to a lesser extent by the Cr/C ratio,

terval strjevanja vpliva predvsem vsebnost ogljika, manj pa razmerje Cr/C in koncentracije ostalih legirnih elementov. Od vsebnosti ogljika, ki sicer znižuje temperaturo tališča, in razmerja Cr/C je odvisen delež karbidne faze v mikrostrukturi, kar tudi vpliva na tališče in interval strjevanja zlitin. Iz faznih diagramov Fe-Cr-C se vidi, da se z naraščajočo vsebnostjo Cr evtektična točka pomika v levo in k višjim temperaturam.

Mikrostruktura zlitin v litem stanju

Mikrostruktura zlitin je odvisna od kemične sestave, razmerja Cr/C in pogojev strjevanja. Vse zlitine smo legirali z Mo, zato imajo v mikrostrukturi poleg primarnih in evtektičnih karbidov M_7C_3 tudi karbide Mo_2C.

Mikrostruktura evtektika je odvisna od deleža avstenitne faze, ki nastaja med procesom strjevanja. Če nastane med strjevanjem veliko avstenita in je majhen delež preostale taline, ki se strdi kot evtektik, imajo evtektični karbidi tendenco, da segregirajo vzdolž kristalnih mej avstenitnih zrn. Take mikrostrukture, ki je značilna za zlitine z do 20 % karbidne faze, pri naših zlitinah, ki imajo od 25 do 35 % karbidne faze, nismo opazili.

V nekaterih zlitinah smo opazili v evtektiku bolj ali manj lamelarno izoblikovane karbide, ki rastejo iz sredine meddendritskih prostorov (sl. 4) Pri drugih zlitinah, pri katerih je avstenitne faze zelo malo in ta praktično ni omejevala strjevanja evtektika, imajo karbidi popolnoma lamelarno obliko (sl. 5). Čeprav so veliki primarni karbidi heksagonalne oblike značilni za litine z nad 35 % karbidne faze, smo te opazili tudi pri nekaterih naših zlitinah, in to predvsem na sredini preizkusnih valjčkov, kjer so bili za njihov nastanek ustreznejši pogoji (sl. 6).

Deleže karbidne faze v mikrostrukturi smo za nekatere zlitine izračunali po enačbi (1):

$$\% K = 12{,}33 \, (\% \, C) + 0{,}55 \, (\% \, Cr) - 15{,}2$$

Izračunane vrednosti se dobro ujemajo z vrednostmi, ki smo jih dobili z meritvami po linearni intercepcijski metodi v optičnem mikroskopu (tabela 2). Vsebnosti Mo in W sta majhni in ne vplivata bistveno na delež karbidne faze.

Tabela 2: Delež karbidne faze (% K) v mikrostrukturi

Zlitina	Cr/C	% C	% Cr	% K izračunan	% K izmerje
7	3,62	3,31	11,97	32,2	30
6	4,80	3,21	15,42	32,9	29
3	5,48	2,72	14,90	26,5	26
5	5,61	3,20	17,95	34,1	35
2	7,39	2,62	19,43	27,9	28
1	7,76	2,49	19,31	26,1	25

Mikrostruktura matice je odvisna od razmerja Cr/C, vsebnosti Mo in pogojev ohlajevanja. Matica ima v litem stanju avstenitno mikrostrukturo, oz. je med ohlajanjem potekla delna ali popolna transformacija avstenita v perlit. Pri litju v kokilo poteka strjevanje in ohlajanje hitreje, kot pri litju v pesek, in perlitna transformacija je zavrta. Pri zlitinah brez Mo lahko pričakujemo popolnoma avstenitno matico pri razmerju Cr/C večjem od 7,2 (1,2). Z legiranjem z Mo se razmerje Cr/C, pri katerem dobimo popolnoma avstenitno matico, pomika proti nižjim vrednostim. To pomeni, da ima lahko litina pri isti vsebnosti Cr več C in zato v mikrostrukturi večji delež karbidne faze in avstenitno matico.

and the concentration of the other alloying elements. The carbon content which namely reduces the melting point, and the Cr/C ratio determine the amount of carbide phase in the microstructure which has also influence on the melting point and the solidification interval of alloys. The Fe-Cr-C phase diagrams show that the increasing Cr content shifts the eutectic point towards the left and to higher temperatures.

Microstructure of As Cast Alloys

Microstructure of alloys depends on the chemical composition, the Cr/C ratio, and the conditions of solidification. All the alloys were alloyed with Mo, thus the microstructure contains also Mo_2C carbides next to the primary and eutectic M_7C_3 carbides.
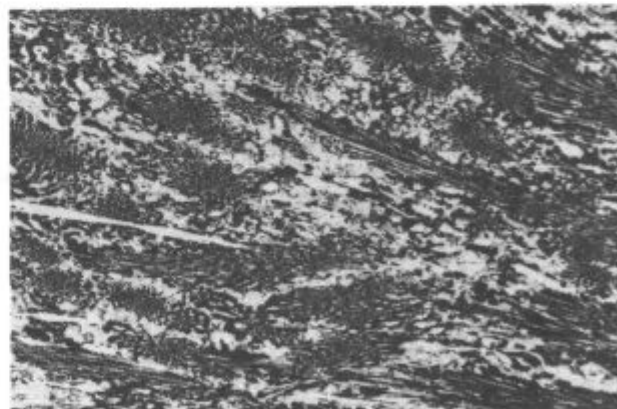
Microstructure of eutectic depends on the amount of austenitic phase which is formed during the solidification. If a high amount of austenite is formed during the solidification, and the portion of the remaining melt which solidifies eutectically is small, the eutectic carbides exhibit tendency to segregate along the boundaries of austenitic grains. Such a microstructure being characteristic for the alloys with up to 20 % of carbide phase was not observed in our alloys which contained 25 to 35 % of carbide phase.

In some alloys more or less lamellar carbides were observed which grow from the centre of interdendritic spaces (Fig. 4). In other alloys with a very low amount of austenitic phase which did not hinder the solidification of eutectic, the carbides exhibited fully lamellar shape (Fig. 5). Though big primary carbides of hexagonal shape are characteristic for the cast irons with over 35 % of carbide phase, they were obseved also in some of our alloys, but mainly in the centre of the testing cylinders where the conditions for their formation were the most suitable (Fig. 6).

The portions of carbide phase in the microstructure was for some alloys evaluated by the equation (1):

$$\% K = 12.33 \, (\% \, C) + 0.55 \, (\% \, Cr) - 15.2$$

The obtained values are in a good agreement with the values which were obtained by the measurements in optical microscope by the intercept method (Table 2). Contents of Mo and W are low and they do not influence essentially the portion of carbide phase.
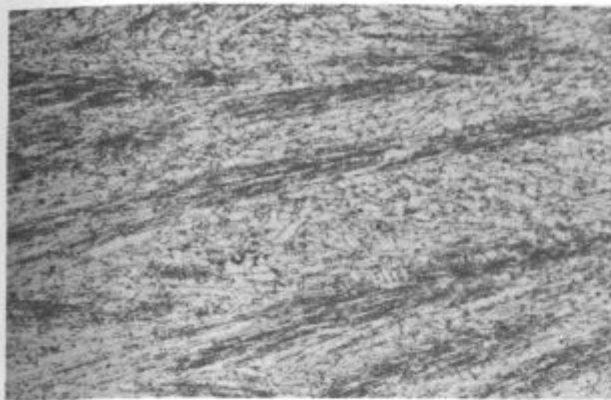

Sl. 4:
Eutektični karbidi rastejo iz sredine meddendritskih prostorov, lito stanje (3,21 % C, 15,42 % Cr, 0,53 % Mo, Cr/C 4,80). Pov. 100×

Fig. 4
Eutectic carbides grow from the centre of interdendritic spaces, as cast (3.21 % C, 15.42 % Cr, 0.53 % Mo, Cr/C 4.80). Magn. 100×

Sl. 5:
Lamelarni eutektični karbidi, lito stanje (3,20 % C, 17,95 % Cr, 0,63 % Mo, Cr/C 5,61). Pov. 100 ×

Fig. 5
Lamellar eutectic carbides, as cast (3.20 % C, 17.95 % Cr, 0.63 % Mo, Cr/C 5.61). Magn. 100 ×

Preiskovane zlitine so legirane z Mo in preizkusni valjčki imajo na presekih, ulitih v kokilo pri razmerjih Cr/C nad 5,5, popolnoma avstenitno matico **(sl. 5)**. Le v večji oddaljenosti od površine smo pri nekaterih vzorcih opazili v mikrostrukturi manjša perlitna zrna. S padajočo vrednostjo razmerja Cr/C narašča v matici delež perlitne faze. Avstenitno perlitna mikrostruktura matice je prikazana na sliki 4.

Perlitno matico lahko reavstenitiziramo in tako zagotovimo, da ima litina po destabilizaciji in transformaciji s stališča mehanskih lastnosti ustreznejšo mikrostrukturo matice (martenzit). Menimo, da z ogrevanjem avstenitno perlitnih litin 50 °C pod solidus temperaturo dobimo avstenitno mikrostrukturo matice. Za natančnejše pogoje reavstenitizacije so v literaturi podani diagrami (1, 2). Vsekakor pa je ugodneje, da z razmerjem Cr/C, legiranjem z Mo in pogoji strjevanja že v litem stanju zagotovimo litini avstenitno mikrostrukturo matice (9).

Kemična sestava karbidov in matice

Koncentracije Cr, Mo, Mn in W v primarnih in evtektičnih karbidih in v matici, izmerjene v elektronskem mikroanalizatorju, so podane v **tabeli 3**. Meritve smo naredili na vzorcih ulitih v kokilo.

Tabela 3: Vsebnosti Cr, Mo, Mn in W v karbidih in matici

Zlitina	Cr/C	% C	% Cr	Mo	Karbidi primarni	Karbidi eutek.	Matica perlit	Matica austenit
7	3.62	3.31	11.97	0.58	38.3 Cr	32.9 Cr	6.7 Cr	—
					0.55 Mo	0.45 Mo	0.26 Mo	—
					0.8 Mn	0.7 Mn	0.6 Mn	—
6	4.80	3.21	15.42	0.53	42.4 Cr	37.0 Cr	7.7 Cr	7.0 Cr
					0.44 Mo	0.46 Mo	0.26 Mo	0.34 Mo
3	5.48	2.72	14.90	0.56	44.8 Cr	39.9 Cr	—	10.5 Cr
					0.97 Mo	0.92 Mo	—	0.13 Mo
					0.9 Mn	0.8 Mn	—	0.7 Mn
5	5.61	3.20	17.95	0.63	48.4 Cr	43.8 Cr	—	10.2 Cr
					0.42 Mo	0.42 Mo	—	0.23 Mo
					0.95 Mn	0.9 Mn	—	0.8 Mn
2	7.39	2.62	19.43	0.52	50.7 Cr	49.0 Cr	—	10.8 Cr
				0.83	0.49 Mo	0.46 Mo	—	0.3 Mo
				W	0.59 W	0.61 W	—	0.44 W
					0.9 Mn	0.9 Mn	—	0.7 Mn
1	7.76	2.49	19.31	0.54	51.2 Cr	49.0 Cr	—	10.5 Cr
					0.41 Mo	0.44 Mo	—	0.31 Mo

V diagramu na sliki 7 je prikazana odvisnost med razmerjem Cr/C v zlitinah in razmerjem Fe/Cr v karbidih

Table 2 Portion of Carbide Phase (% K) in the Microstructure

Alloy	Cr/C	% C	% Cr	% K calculated	% K measured
7	3.62	3.31	11.97	32.2	30
6	4.80	3.21	15.42	32.9	29
3	5.48	2.72	14.90	26.5	26
5	5.61	3.20	17.95	34.1	35
2	7.39	2.62	19.43	27.9	28
1	7.76	2.49	19.31	26.1	25

Microstructure of matrix depends on the Cr/C ratio, amount of Mo, and conditions of solidification. Matrix as cast has austenitic microstructure, or a partial or complete transformation of austenite into pearlite occured during the solidification. Solidification and cooling are faster in casting into moulds than in casting into sand, and pearlitic transformation is retarded. In alloys without Mo fully austenitic matrix can be expected at the Cr/C ratios higher than 7.2 (1, 2). Alloying with Mo shifts the Cr/C ratio at which fully austenitic matrix is obtained towards lower values. This means that cast iron can contain at the same Cr more C, and thus a greater portion of carbide phase can be in the microstructure.

Investigated alloys were alloyed with Mo, and the testing cylinders exhibit on the cross sections cast into mould a fully austenitic matrix if Cr/C ratio was over 5.5 **(Fig. 5)**. Only at a greater distance from the surface smaller pearlitic grains were observed in the microstructure of some samples. The reduced Cr/C ratio causes an increased amount of pearlitic phase in the matrix. The austenitic-pearlitic microstructure of the matrix is shown in Fig. 4.
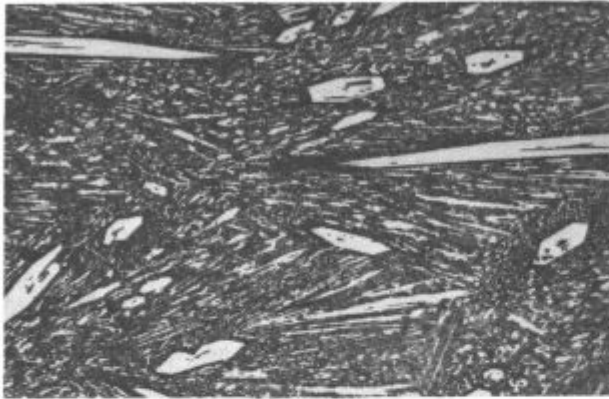
Pearlitic matrix can be reaustenitized, and thus it is ensured that the cast iron has a more suitable microstructure of matrix (martensite) from the viewpoint of mechanical properties after the destabilization and the transformation. It is supposed that heating austenitic-pearlitic cast iron at 50° C below the solidus temperature gives austenitic microstructure of the matrix. More detailed conditions of reaustenitization are given in graphs in references (1, 2). Anyhow, it is more favourable to ensure the austenitic microstructure of the matrix in the as cast alloy by the Cr/C ratio, alloying with Mo, and the conditions of solidification.

Chemical Composition of Carbides and of Matrix

Concentrations of Cr, Mo, Mn, and W in the primary and the eutectic carbides, and in the matrix, measured by the electron microanalyzer are presented in **Table 3**.

Table 3 Contents of Cr, Mo, Mn, and W in Carbides and in the Matrix

Alloy	Cr/C	% C	% Cr	Mo	Carbides Primary	Carbides Eutec.	Matrix Pearlite	Matrix Austen.
7	3.62	3.31	11.97	0.58	38.3 Cr	32.9 Cr	6.7 Cr	—
					0.55 Mo	0.45 Mo	0.26 Mo	—
					0.8 Mn	0.7 Mn	0.6 Mn	—
6	4.80	3.21	15.42	0.53	42.4 Cr	37.0 Cr	7.7 Cr	7.0 Cr
					0.44 Mo	0.46 Mo	0.26 Mo	0.34 Mo
3	5.48	2.72	14.90	0.56	44.8 Cr	39.9 Cr	—	10.5 Cr
					0.97 Mo	0.92 Mo	—	0.13 Mo
					0.9 Mn	0.8 Mn	—	0.7 Mn
5	5.61	3.20	17.95	0.63	48.4 Cr	43.8 Cr	—	10.2 Cr
					0.42 Mo	0.42 Mo	—	0.23 Mo
					0.95 Mn	0.9 Mn	—	0.8 Mn
2	7.39	2.62	19.43	0.52	50.7 Cr	49.0 Cr	—	10.8 Cr
				0.83	0.49 Mo	0.46 Mo	—	0.3 Mo
				W	0.59 W	0.61 W	—	0.44 W
					0.9 Mn	0.9 Mn	—	0.7 Mn
1	7.76	2.49	19.31	0.54	51.2 Cr	49.0 Cr	—	10.5 Cr
					0.41 Mo	0.44 Mo	—	0.31 Mo

Sl. 6:
Primarni karbidi heksagonalne oblike. Pov. 100×
Fig. 6
Primary carbides of hexagonal shape. Magn. 100×

M_7C_3. Z razmerjem Fe/Cr je podana sestava karbidov M_7C_3, ki se sicer lahko spreminja od $(Cr_2Fe_5) C_3$ do $(Cr_5Fe_2)C_3$. Primarni in evtektični karbidi imajo v naših zlitinah sestavo od malo nad stehiometričnim razmerjem $(Cr_3Fe_4) Cr_3$ do $(Cr_4Fe_3) C_3$. Krivulja za evtektične karbide leži nad krivuljo za primarne karbide, ker imajo evtektični karbidi pri istih vrednostih Cr/C manjšo vsebnost Cr. Razlika v vsebnosti Cr med primarnimi in evtektičnimi karbidi je največja pri najnižjem razmerju Cr/C. Z naraščajočo vsebnostjo tega razmerja proti 8 se vsebnost Cr v primarnih in evtektičnih karbidih približuje isti vrednosti.

Poleg Cr, ki v kristalni mreži karbidov nadomešča atome Fe, smo v karbidih izmerili tudi določene koncentracije Mo, Mn in W. Vsebnost Mo v zlitinah je majhna, zato je v mikrostrukturi malo karbidov Mo_2C. Ti karbidi so drobni, vendar smo jih lahko določili v elektronskem mikroanalizatorju, kot tudi karbide W v zlitinah, legiranih s tem elementom.

Vsebnost Cr v matici narašča z vrednostjo razmerja Cr/C. Meritve koncentracij Cr in Mo v matici so pokazale, da je ta zelo nehomogena (5). Odstopanja od povprečnih vrednosti so pri Cr v mejah ±20 %. Bistveno večje je izcejanje Mo, in sicer večinoma v mejah ±50 %. V nekaterih primerih pa smo v izcejah izmerili tudi do 2 % Mo. Podobno smo ugotovili, da tudi karbidi nimajo homogene sestave. Pri večjih, predvsem primarnih karbidih, je koncentracija Cr največja v sredini in se zmanjšuje proti robu karbidnega zrna.

V karbidih smo merili koncentracije Cr, Mo in W tudi na vzorcih, žarjenih 2, 4 in 8 ur na temperaturi 1050 °C. Pri tej temperaturi poteka izločanje sekundarnih karbidov in s tem destabilizacija avstenitne matice. Izmerjene razlike v koncentraciji omenjenih elementov med litim in žarjenim stanjem niso sistematične in so odstopanja v mejah merilnih napak.

Diagram izotermne destabilizacije avstenita

Sistematične preiskave destabilizacije avstenita, izotermna transformacijska diagrama za nedestabiliziran in destabiliziran avstenit (TTT) in kontinuirni transformacijski diagram za destabiliziran avstenit (CTT) smo naredili za zlitino 5 z naslednjo kemično sestavo: 3,2 % C, 1,22 % Si, 0,86 % Mn, 0,035 % S, 0,030 % P, 17,95 % Cr, 0,63 % Mo, 0,69 % Ni, 0,08 % Ti in 0,095 % V. Zlitina ima razmerje Cr/C 5,61 in v litem stanju avstenitno matico (sl. 5). Izotermna transformacijska diagrama smo naredili na osnovi metalografskih

Sl. 7:
Odvisnost med razmerjem Cr/C in razmerjem Fe/Cr v karbidih M_7C_3
Fig. 7
Relation between the Cr/C ratio and Fe/Cr ratio in M_7C_3 carbides

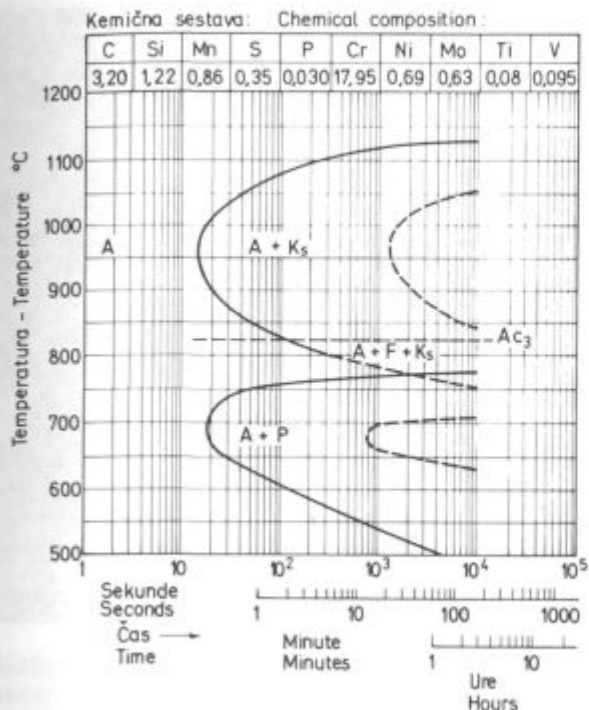Measurements were made on the samples cast into mould.

Plot in **Fig. 7** gives the relationship between the Cr/C ratio in alloys and the Fe/Cr ratio in M_7C_3 carbides. The Fe/Cr ratio defines the composition of M_7C_3 carbides which varies between $(Cr_2Fe_5)C_3$ and $(Cr_5Fe_2)C_3$. Primary and eutectic carbides in our alloys have the composition between the composition which is slightly above the stoichiometric one of $(Cr_3Fe_4)C_3$, and the composition of $(Cr_4Fe_3)C_3$. The curve for eutectic carbides is above the curve for primary carbides since eutectic carbides at equal Cr/C ratios have smaller contents of Cr. The difference in Cr content between the primary and the eutectic carbides was the highest at the lowest Cr/C ratio. If this ratio goes towards 8, the Cr content in primary and eutectic carbides approaches to the same value.

Beside Cr which in crystal lattice of carbides substitutes Fe atoms, certain concentrations of Mo, Mn, and W were found in carbides. Mo content in alloys is small therefore the microstructure contains small amount of Mo_2C. These carbides are fine but they were determined by the electron microanalizer, as well as the tungsten carbides in the alloys alloyed with that element.

Cr content in matrix is increased with the increased Cr/C ratio. Measurements of Cr and Mo concentrations in the matrix showed that matrix is very unhomogeneous (5). Deviations from the mean values are for Cr in the limits ±20 %. Essentially greater are segregations of Mo, mainly in limits ±50 %. In some cases in segregations, even up to 2 % Mo was found. Similarly, it was found that also carbides do not have a homogeneous composition. In bigger, mainly primary carbides the concentration of Cr is the greatest in the centre and it is reduced towards the edge of the carbide grain.

In carbides, the concentrations of Cr, Mo, and W were measured also in the samples annealed 2, 4 and 8 hours at 1050° C. At this temperatures secondary carbides are precipitated and thus the austenitic matrix is

Kemična sestava: Chemical composition :

C	Si	Mn	S	P	Cr	Ni	Mo	Ti	V
3,20	1,22	0,86	0,35	0,030	17,95	0,69	0,63	0,08	0,095

Sl. 8:

Diagram izotermne destabilizacije avstenita (A — austenit, F — ferit, P — perlit, K$_s$ — sekundarni karbidi)

Fig. 8

Diagram of isothermal destabilization of austenite (A — austenite, F — ferrite, P — pearlite, K$_s$ — secondary carbides)

preiskav. Mikrostrukturne spremembe smo opredelili v optičnem mikroskopu in v SEM. V nekaterih primerih, ko je bilo težko določiti mikrostrukturne komponente, smo si pomagali še z meritvami mikrotrdot in selektivnim jedkanjem (15, 16).

Za izdelavo diagrama izotermne destabilizacije avstenita smo vzorce izotermno žarili različno dolgo časa v temperaturnem področju med 500 in 1150° C. Razpad avstenita poteka v dveh temperaturnih področjih, ki se v ozkem področju prekrivata **(sl. 8)**. Za toplotno obdelavo zlitin je pomembna destabilizacija avstenita z izločanjem sekundarnih karbidov (K$_s$), ki poteka v višjem temperaturnem področju. Izločanje sekundarnih karbidov je najhitrejše med 940 in 990 °C. Nad temperaturo Ac$_3$ poteka transformacija $\gamma = \gamma + K_s$ in pod to temperaturo $\gamma = \gamma + \alpha + K_s$.

Nad temperaturo Ac$_3$ se iz avstenita izločajo karbidi M$_7$C$_3$. V temperaturnem področju med Ac$_3$ in Ac$_1$ pa se iz avstenita izločajo tudi karbidi M$_{23}$C$_6$ (10). Izločanje sekundarnih karbidov je za nadaljnjo toplotno obdelavo bistvenega pomena. Brez predhodne destabilizacije, pri kateri se zaradi izločanja sekundarnih karbidov v avstenitu zmanjša vsebnost Cr in C, transformacija avstenita v martenzit, kot tudi v bainit, niti ni mogoča. Perlitna transformacija pa poteka v destabiliziranem avstenitu počasneje.

V nižjem temperaturnem področju razpada poteka transformacija avstenitne matice v perlit. Transformacija poteka najhitreje med 670 in 710 °C.

Sekundarni karbidi se začnejo izločati iz avstenita po določeni inkubacijski dobi, in to ob kristalnih mejah med avstenitnimi zrni in na meji avstenitnih zrn z evtektičnimi karbidi. Proti sredini avstenitnih zrn poteka izločanje hitreje po določenih kristalografskih ravninah **(sl. 9, 10, 11)**. V začetni fazi izločanja so karbidi drobni,

destabilized. The measured differences of concentrations of the mentioned elements between the cast and annealed state are not systematic, and the deviations are in the limits of measuring errors.
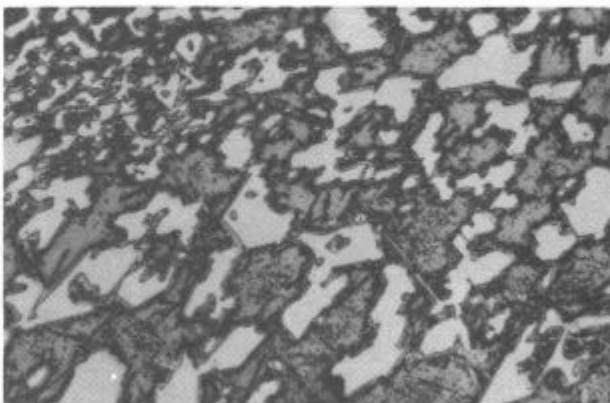
Diagram of Isothermal Destabilization of Austenite

Systematic investigations of the destabilization of austenite, isothermal transformation diagrams for undestabilized and destabilized austenite (TTT), and the continuous transformation diagram for destabilized austenite (CTT) were constructed for the alloy 5 with the following composition: 3.2 % C, 1.22 % Si, 0.86 % Mn, 0.035 % S, 0.030 % P, 17.95 % Cr, 0.63 % Mo, 0.69 % Ni, 0.08 % Ti, and 0.095 % V. The Cr/C ratio of the alloy was 5.61, and the as cast alloy exhibits austenitic matrix **(Fig. 5)**. The isothermal transformation diagrams were constructed from data of metallographic investigations. Microstructural variations were determined in optical microscope and by SEM. In some cases when the microstructural components were not easy to be determined, measurements of microhardnesses, and selective etching were applied (15, 16).

To construct the diagram of isothermal destabilization of austenite, the samples were isothermally annealed for various times in the temperature interval 500 to 1150° C. Decomposition of austenite occurs in two temperature intervals which overlap in a narrow region **(Fig. 8)**. The destabilization of austenite with precipitation of secondary carbides (K$_s$) occuring in the higher temperature interval is important for the heat treatment of alloys. Precipitation of secondary carbides is the fastest between 940 and 990° C. Above Ac$_3$ transformation $\gamma = \gamma + K_s$ takes place, and below that point $\gamma = \gamma + \alpha + K_s$.

Above Ac$_3$ M$_7$C$_3$ carbides are precipitated from austenite. In the temperature interval between Ac$_3$ and Ac$_1$ also M$_{23}$C$_6$ carbides are precipitated from austenite (10). Precipitation of secondary carbides is essential for further heat treatment. Without the predestabilization when due to the precipitation of secondary carbides the concentrations of Cr and C are reduced, the transformation of austenite into martensite as well as into bainite is not possible. Pearlitic transformation is slower in the destabilized austenite.

In the lower temperature interval of the decomposition, the transformation of austenitic matrix into pearlite takes place. It is the fastest between 670 and 710° C.

Sl. 9:

Izločanje sekundarnih karbidov v avstenitu, 80 s žarjeno na 1050°C. Pov. 500 ×

Fig. 9

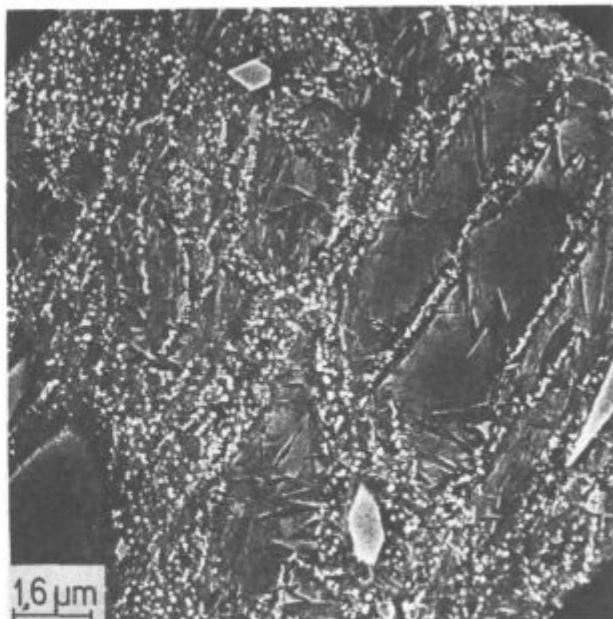Precipitation of secondary carbides in austenite, annealed 80 s at 1050° C. Magn. 500 ×

Sl. 10:
Morfologija izločanja sekundarnih karbidov iz avstenita, 40 s žarjeno na 1050°C (matica je iz avstenita in martenzita)
Fig. 10
Morphology of precipitation of secondary carbides from austenite, annealed 40 s at 1050° C (Matrix is of austenite and martensite)
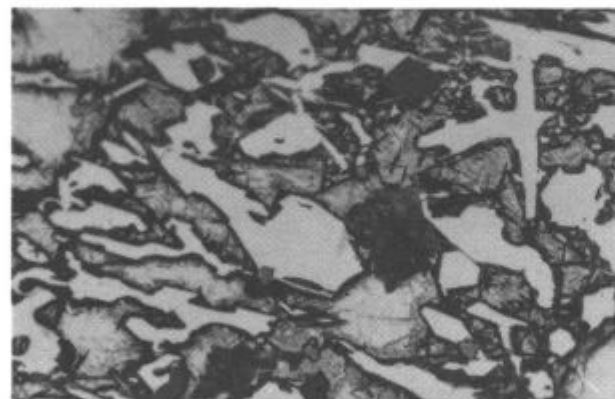

Sl. 11:
Morfologija izločanja sekundarnih karbidov iz avstenita, 5 min žarjeno na 950°C (matica je iz avstenita in martenzita)
Fig. 11
Morphology of precipitation of secondary carbides from austenite, annealed 5 min. at 950° C (Matrix is of austenite and martensite)

s časom izotermnega žarjenja pa rastejo. Največji vpliv na rast sekundarnih karbidov ima temperatura in nad 1050 °C je njihova rast že zelo hitra.

Inkubacijski čas za potek premene v perlitnem področju je daljši. Morfologija izločanja cementita je podobna kot pri izločanju sekundarnih karbidov, le izločanje cementita po prednostnih kristalografskih ravninah je manj izrazito. Sam potek transformacije je hitrejši kot proces destabilizacije. Na nekaterih mestih se vidi, da je transformacija potekla hitro po celem zrnu avstenita (sl. 12). Oblika cementitnih lamel in medlamelarna razdalja v perlitu sta odvisni od temperature transformacije. Pri 750 °C je cementit grob in globularen, le na sredini večjih zrn je nakazana lamelarna oblika. S padajočo temperaturo transformacije ima cementit vedno bolj lamelarno obliko (sl. 13, 14). Najmanjšo

Sl. 12:
Perlitna transformacija, 5 min žarjeno na 690°C. Pov. 500 ×
Fig. 12
Pearlitic transformation, annealed 5 min. at 690° C, Magn. 500 ×

Secondary carbides start to precipitate from austenite after a certain induction period, and this occurs on the grain boundaries between the austenite grains, and on the boundaries of austenite grains with eutectic carbides. Towards the centre of austenite grains the precipitation is faster on certain crystallographic planes (Figs. 9, 10, and 11). In the initial phase of precipitation, the carbides are fine, but they grow with the time of isothermal annealing. The greatest influence on the growth of secondary carbides has the temperature, and above 1050° C their growth is already very fast.

Induction period for the transformation in the pearlitic region is longer. Morphology of cementite precipitation is similar to that of the secondary carbides, only precipitation of cementite on the preferred crystalographic planes is less pronounced. Transformation itself is faster than the process of destabilization. On same spots it is evident that the transformation was fast through the whole austenite grain (Fig. 12). The shape of cementite lamellae and the interlamellar spacing in perlite depend on the transformation temperature. At 750° C cementite is coarse and globular, only in the centre of bigger grains lamellar formation is indicated. With decreasing temperature of transformation the shape of cementite is becoming more lamellar (Figs. 13 and 14). The smallest interlamellar spacing in pearlite is found in the alloys at the transformation temperature around 650° C. At lower temperatures pearlitic transformation is slower, and lamellae can be observed only after longer annealing times.

The curves of the initial precipitation of secondary carbides, and of pearlitic transformation were metallographically exactly determined by optical microscopy and by SEM. Bigger problem was to determined the time when both processes are completed. Precipitation of carbides and the pearlitic transformation move from the grain boundaries into the interior of the grains. The time
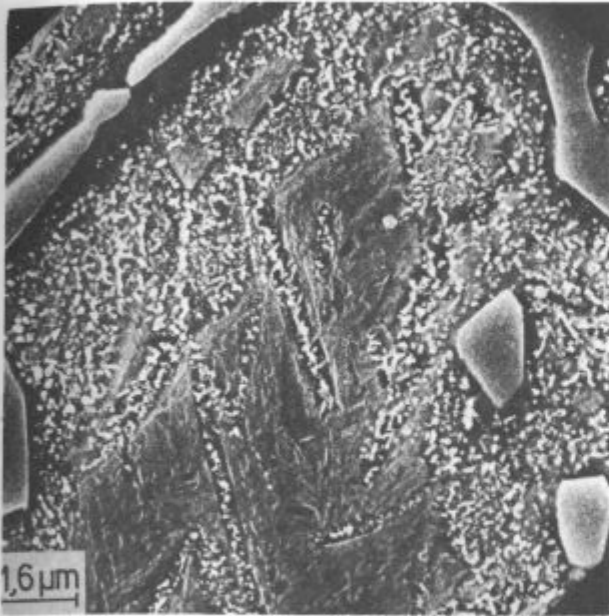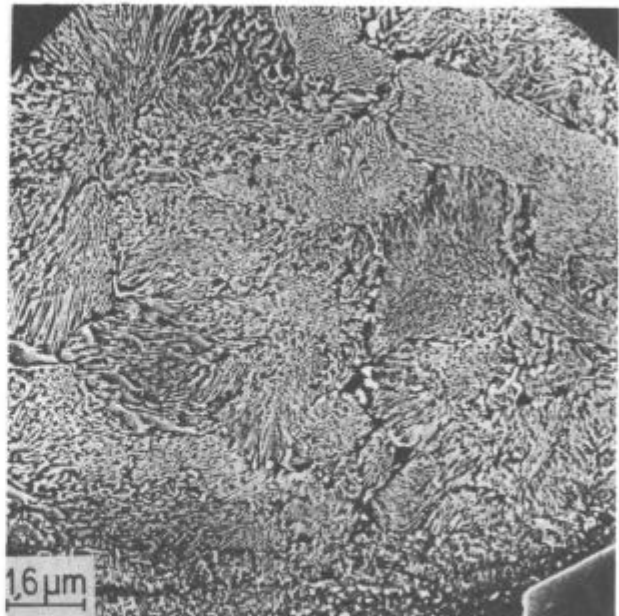
Sl. 13:
Morfologija perlitne transformacije, 10 min žarjeno na 750° C
Fig. 13
Morphology of pearlitic transformation, annealed 10 min. at 750° C

Sl. 14:
Morfologija perlitne transformacije, 120 min žarjeno na 650° C
Fig. 14
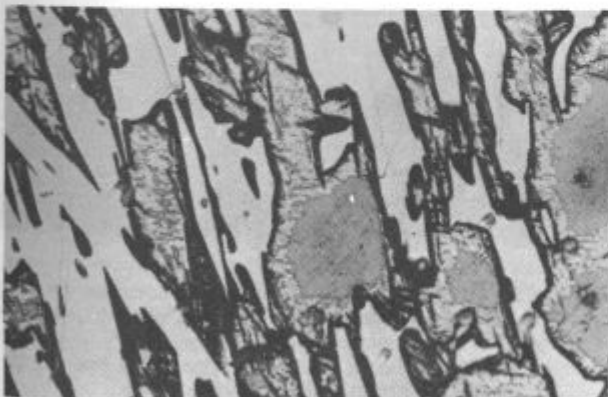Morphology of pearlitic transformation, annealed 120 min. at 650° C

medlamelarno razdaljo v perlitu ima zlitina v temperaturnem področju transformacije okoli 650 °C. Pri nižjih temperaturah poteka perlitna transformacija počasneje in lamele opazimo le pri daljših časih žarjenja.

Krivulji začetka izločanja sekundarnih karbidov in perlitne transformacije smo lahko metalografsko točno določili z optičnim mikroskopom in v SEM. Večji problem je določiti čas, v katerem sta oba procesa končana. Izločanje karbidov in perlitna transformacija potekata s kristalnih mej v notranjost zrn. Čas, v katerem je proces končan, je zato odvisen od velikosti kristalnih zrn. V nekaterih primerih tudi sicer težko točno opredelimo konec procesa izločanja sekundarnih karbidov, ker v martenzitni osnovi težko ločimo karbidna zrna. Z meritvami trdote si prav tako težko pomagamo, saj se trdota, ko je izločenih že več kot 80 % sekundarnih karbidov, ali se perlitna transformacija približuje koncu, bistveno ne spremeni in so odstopanja v mejah merilnih napak. Na potek destabilizacije in perlitne transformacije pa vpliva tudi izcejanje legirnih elementov. Iz teh razlogov sta krivulji, ki označujeta konec obeh procesov, opredeljeni le približno.

of the process termination thus depends on the size of crystal grains. In some cases the exact determination of the end of the precipitation of secondary carbides is difficult since carbide grains can hardly be distinguished in the martensitic matrix. Measurements of hardness can also not help since the hardness changes very little when more than 80 % of secondary carbides are precipitated or the pearlitic transformation approaches to its end, and the deviations are in the limits of measuring errors. The destabilization process and the pearlitic transformation are influenced also by the segregations of alloying elements. Therefore the curves determining the completion of both processes are approximate.

In some samples being destabilized below 900° C also retained austenite was observed in the microstructure. Due to fast cooling (microstructure was stabilized by quenching) beside the stable austenite also residual austenite is present in the microstructure of the matrix in partial destabilization. The both austenites differ in the content of alloying elements (Cr, Mo, and C) **(Fig. 15)**.

The Ac_3 point was determined dilatometrically.

Sl. 15:
Delno destabiliziran avstenit (850° C, 2 min). V sredini zrn je stabilni avstenit. Ob kristalnih mejah, kjer so se izločili sekundarni karbidi, je med martenzitnimi iglami zaostali avstenit.
Pov. 500 ×
Fig. 15
Partially destabilized austenite (850° C, 2 min.). In the centre of grains there is stable austenite. On grain boundaries where secondary carbides are precipitated there is residual austenite between the martensitic needles. Magn. 500 ×

Pri nekaterih vzorcih, destabiliziranih pri temperaturah pod 900 °C, smo opazili v nikrostrukturi tudi zaostali avstenit. Zaradi hitrega ohlajanja (mikrostrukturo smo stabilizirali z gašenjem) je v mikrostrukturi matice pri delni destabilizaciji prisoten poleg stabilnega avstenita še zaostali avstenit. Avstenita se razlikujeta po vsebnosti legirnih elementov Cr, Mo in C (sl. 15).

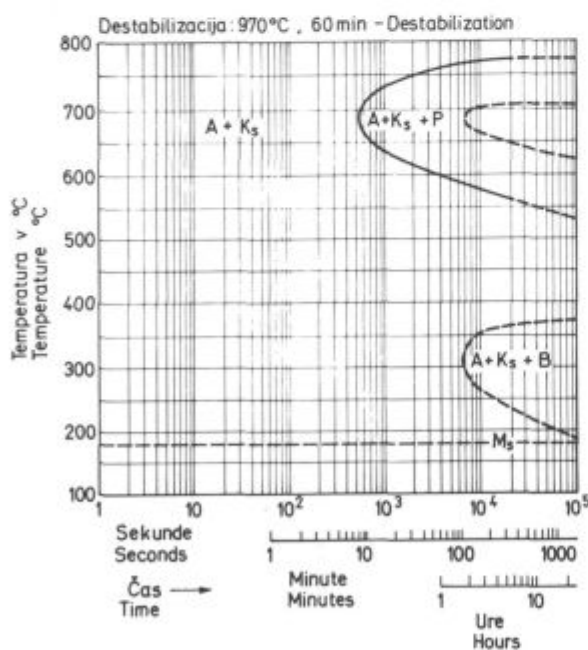Temperaturo Ac_3 smo določili z dilatometrom.

Izotermni transformacijski diagram za destabiliziran avstenit.

Temperatura destabilizacije 970 °C je istočasno izhodna temperatura nadaljnje toplotne obdelave.

Omenili smo že, da višje razmerje Cr/C in legiranje z Mo zavirata transformacijo avstenita v perlit. Pri destabiliziranem avstenitu moramo upoštevati še vpliv sekundarnih karbidov.

V primerjavi s TTT diagramom za nedestabiliziran avstenit je pri destabiliziranem avstenitu področje nastajanja perlita pomaknjeno močno v desno, v temperaturah pa ni nobene razlike. Več je v avstenitu izločenih sekundarnih karbidov, daljša je inkubacijska doba. Za praktično uporabo diagrama je seveda pomembna le popolna destabilizacija avstenita (sl. 16).

Določena razlika je v morfologiji nastajanja perlita. V nedestabiliziranem avstenitu poteka transformacija predvsem s kristalnih mej proti sredini avstenitnih zrn. Pri destabiliziranem avstenitu poteče premena hitro po celem, oziroma delu avstenitnega zrna. S časom žarjenja narašča število transformiranih kristalnih zrn. (sl. 17). Sekundarni karbidi delujejo kot kali in v destabiliziranem avstenitu poteka kontinuirna transformacija (sl. 18). Tudi pri teh pogojih transformacije je iz že omenjenih razlogov nemogoče točno opredeliti konec premene.

Isothermal Transformation Diagram for Destabilized Austenite

The destabilization temperature of 970° C is simultaneously the starting temperature for further heat-treatment processes.
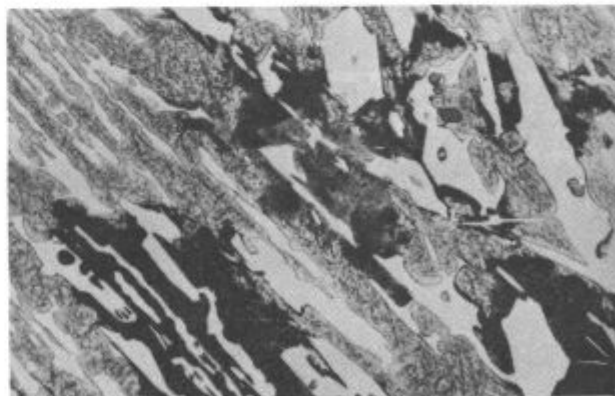
It was already mentioned that higher Cr/C ratio and alloying with Mo retard the transformation of austenite into pearlite. In destabilized austenite also the influence of secondary carbides must be taken in account.

Compared to the TTT diagram for understabilized austenite the region of formation of pearlite in destabilized austenite is shifted significantly to the right while there are no differences related to the temperatures. Amount of secondary carbides precipitated in austenite is greater, longer is also the induction period. Only the complete destabilization of austenite (Fig. 16) is certainly important for practical application of the diagram.

There is a certain difference in the morphology of pearlite formation. In undestabilized austenite the transformation goes mainly from crystal boundaries towards the centre of austenite grains. In destabilized austenite the transformation is fast over the whole or over a part of austenite grain. Longer annealing time increases the number of transformed crystal grains (Fig. 17). Secondary carbides are nuclei, and continuous transformation takes place in destabilized austenite (Fig. 18). Also in these conditions of transformation it is not possible to determine exactly the termination of the transformation due to the reasons already mentioned.

Formation of cementite is influenced also by secondary carbides beside the temperature of isothermal transformation. They are bigger in the bigger austenite grains, but their density is lower. Thus the growth of cementite in the bigger grains is less hindered than in the smaller ones.

Bainitic transformation is possible only after the destabilization of austenite and at Cr/C ratios smaller than 5.2. By alloying with Mo, bainite can be obtained also at higher concentrations of Cr (1, 6). Induction period for the bainitic transformation is long. Significant portion of bainitic phase in the microstructure is obtained only after longer times of isothermal annealing. A completely bainitic matrix can be expected only after a very long times of isothermal annealing when the alloy has a suitable Cr/C ratio and is alloyed with Mo.
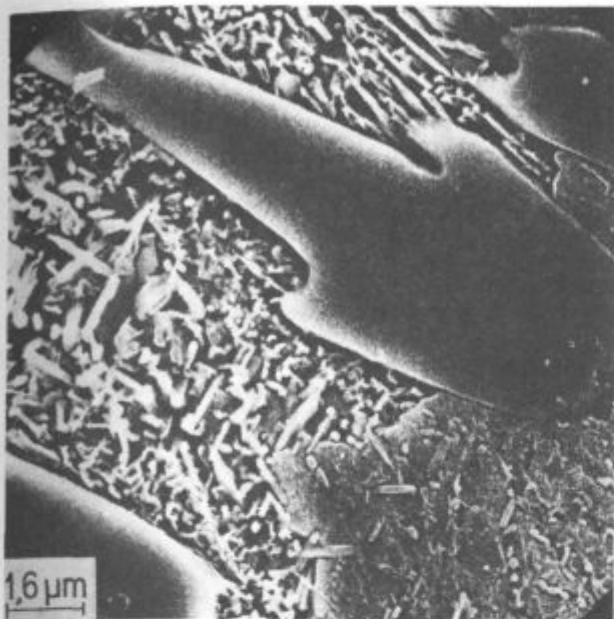

Sl. 16:
Izotermni transformacijski diagram za destabiliziran avstenit (A — avstenit, K_s — sekundarni karbidi, P — perlit, B — bainit)

Fig. 16
Isothermal transformation diagram for destabilized austenite (A — austenite, K — secondary carbides, P — pearlite, B — bainite)

Sl. 17:
Perlitna transformacija destabilizirane avstenitne matice, 60 min žarjeno na 650°C. Pov. 500×

Fig. 17
Pearlitic transformation of destabilized austenitic matrix, annealed 60 min. at 650° C. Magn. 500×
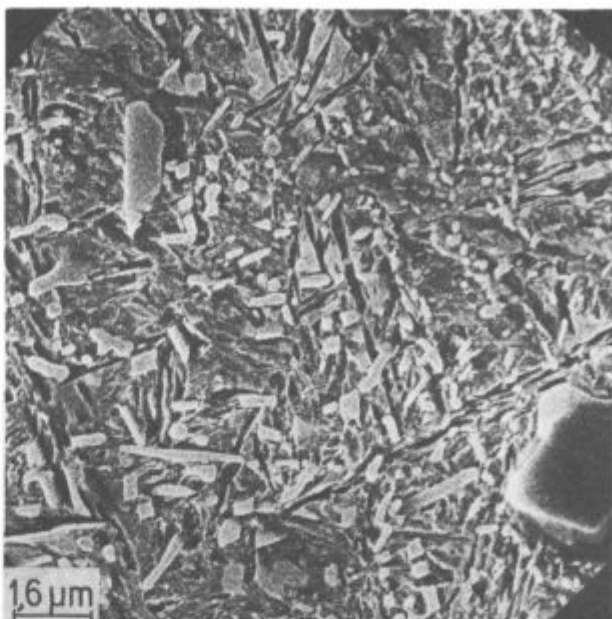
Sl. 18:
Meja med perlitnim zrnom (temnejše) in netransformiranim avstenitom (svetlejše) v destabilizirani matici

Fig. 18
Boundary between the pearlite grain (darker) and not transformed austenite (brighter) in the destabilized matrix

Sl. 19:
Morfologija bainitne transformacije v destabiliziranem avstenitu (300°C, 4 ure). Mikrostruktura matice je iz avstenita, bainita, martenzita in sekundarnih karbidov

Fig. 19
Morphology of bainitic transformation in destabilized austenite (300°C, 4 hours). Micostructure of matrix is of austenite, bainite, martensite, and secondary carbides

Na izoblikovanje cementita vplivajo poleg temperature izotermne transformacije še sekundarni karbidi. Ti so v večjih avstenitnih zrnih večji, njihova gostota pa je manjša. Zato je v večjih zrnih rast cementita manj ovirana, kot v manjših.

Bainitna transformacija je možna le po destabilizaciji avstenita in razmerjih Cr/C manjših od 5,2. Z legiranjem zlitin z Mo lahko dobimo bainit tudi pri višjih koncentracijah Cr (1,6). Inkubacijska doba za potek bainitne premene je dolga. Pomemben delež bainitne faze v mikrostrukturi dobimo le pri daljših časih izotermnega žarjenja. Popolnoma bainitno matico pa lahko pričakujemo po zelo dolgih časih žarjenja zlitin z ustreznim razmerjem Cr/C in legiranih z Mo.

Bainitno in martenzitno mikrostrukturo lahko ločimo le v SEM (17). Bainit stabilizira avstenit, zato je v mikrostrukturi matice še precej netransformiranega avstenita (sl. 19). To so potrdile tudi meritve mikrotrdot.

Začetek martenzitne transformacije smo določili z dilatometrom. M_s temperatura za popolnoma destabilizirano zlitino (970 °C, 60 min) je 180 °C. Potek martenzitne transformacije ni odvisen le od delne ali popolne destabilizacije, temveč tudi od temperature destabilizacijskega žarjenja. M_s temperatura se znižuje z naraščajočo temperaturo destabilizacije (1, 6, 7). Pri kaljenju delno destabiliziranega avstenita je v matici poleg martenzita tudi avstenit.

Kontinuirni transformacijski diagram za destabiliziran avstenit

Diagram, prikazan na **sliki 20** velja za popolnoma destabilizirano zlitino (970 °C, 30 min). Preizkuse smo naredili tudi pri drugih temperaturah destabilizacije in na delno destabiliziranih vzorcih, da smo dobili čim več podatkov o vplivu različnih pogojev destabilizacije na mikrostrukturne značilnosti pri kontinuirnem ohlajanju.

Bainitic and martensitic microstructure can be distinguished only by SEM (17). Bainite stabilizes austenite therefore a good deal of not transformed austenite can be found in the microstructure of the matrix **(Fig. 19)**. This was confirmed also by the microhardness measurements.
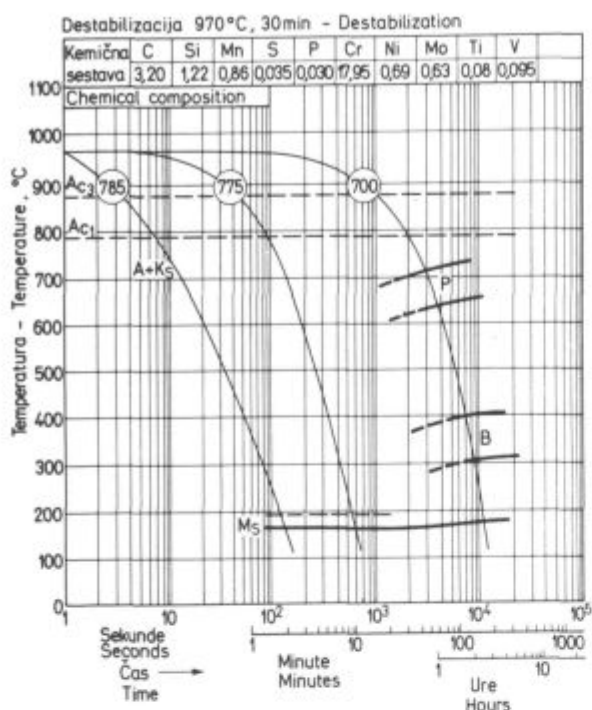
The beginning of the martensitic transformation was determined by dilatometer. M_s point for a completely destabilized alloy (970° C, 60 min.) is at 180° C. Course of martensitic transformation does not depend only on the partial or complete destabilization but also on the temperature of the destablization annealing. M_s temperature is lowered with the increasing temperature of destabilization (1, 6, 7). After hardening the partially destabilized austenite, also austenite next to the martensite is found in the matrix.

Continuous Transformation Diagram for Destabilized Austenite

Diagram is presented in **Fig. 20** and it is valid for a completely destabilized alloy (970° C, 30 min.). Experiments were made also at other temperatures of destabilization, and with partially destabilized samples in order to obtain the most possible data about the influences of various conditions of destabilization on the microstructural characteristics in continuous cooling.

In slow cooling at 300° C/h, the transformation occurs at first in pearlitic stage, then also in the bainitic stage. The extent of transformation is in both stages approximately equal. Martensitic transformation is namely observed, but amount of formed martensitic phase is small. At shorter times of destabilization the extent of transformation in pearlitic stage is smaller and in the bainitic one greater, but at temperatures around 200° C also martensitic transformation is observed.

Destabilizacija 970°C, 30min – Destabilization

Kemična sestava	C	Si	Mn	S	P	Cr	Ni	Mo	Ti	V
Chemical composition	3,20	1,22	0,86	0,035	0,030	17,95	0,69	0,53	0,08	0,095

Sl. 20:

Kontinuirni transformacijski diagram za destabiliziran avstenit (A — avstenit, K_s — sekundarni karbidi, P — perlit, B — bainit)

Fig. 20

Continuous transformation diagram for destabilized austenite (A — austenite, K_s — secondary carbides, P — pearlite, B — bainite)

Pri počasnem ohlajevanju 300 °C/h pride do premene najprej v perlitni, nato pa v bainitni stopnji. Obseg transformacije je v obeh stopnjah približno enak. Martenzitna premena se sicer opazi, martenzitne faze pa je nastalo malo. Pri krajših časih destabilizacije je obseg tranformacije v perlitni stopnji manjši, v bainitni pa večji, s tem da se pri temperaturah okrog 200 °C opazi tudi martenzitna premena.

Pri večjih hitrostih ohlajanja (merjeno v sekundah ohlajanja med 800 in 500°C, oznaka t8/5) dobimo pri hitrosti t8/5 = 165 s že popolnoma martenzitno premeno. V začetku premene martenzitne premene smo opazili anomalijo (črtkana krivulja M_s). Podobni rezultati iz literature to anomalijo omenjajo, vendar brez ustrezne razlage. Ugotavljamo pa, da je anomalija pri krajših časih destabilizacije bolj izrazita.

Naša preizkušanja so bila izvedena v omejenem obsegu, vendar se vidi, da ima čas destabilizacije, ki vpliva na obseg izločanja sekundarnih karbidov, bistveno vlogo na transformacijo avstenita pri kasnejšem ohlajevanju. Večja stopnja destabilizacije avstenita pospešuje obseg transformacije v perlitni stopnji. Anomalija pri martenzitni premeni, ki je večja pri manjši destabilizaciji avstenita, je verjetno povezana z nehomogenostjo avstenita. Ta je vsekakor večja pri nepopolni destabilizaciji.

Premenske točke, ki so vrisane na diagramu, smo določili na podlagi dilatometrskih krivulj pri kontinuirnem ogrevanju s hitrostjo 300 °C/h.

Mikrostruktura matice je odvisna od hitrosti ohlajanja. Pri delni destabilizaciji je v sredini kristalnih zrn še avstenit.

At higher cooling rates (measured in seconds for cooling from 800 to 500° C, marked by t8/5) a complete martensitic transformation is obtained at the rate t8/5 = 165 s. In the beginning of the martensitic transformation an anomaly was observed (dashed curve M_s). Similar results in references mention this anomaly but without any explanation. It was found that the anomaly is more pronounced at shorter times of destabilization.

Our testing was limited but it is evident that the time of destabilization which influences the extent of secondary-carbide precipitation has an essential role in the transformation of austenite at further cooling. Higher stage of austenite destabilization accelerates the extent of transformation in the pearlitic stage. The anomaly in the martensitic transformation which is greater at smaller destabilization of austenite is probably connected with the unhomogeneity of austenite. This is anyhow greater at uncomplete destabilization.

Transformation points being plotted into the diagram were determined from dilatometric curves in continuous heating at the rate 300° C/h.

The microstructure of the matrix depends on the cooling rate. In partial destabilization still austenite is found in the centre of crystal grains.

Residual austenite can be obtained at harsher conditions of hardening and at higher contents of Mn and Ni.

Morphology of pearlite depends on the degree of destabilization as it was already explained at the isothermal conditions of the transformation.

Hardness of Alloys

Corresponding applicable properties of white chromium cast irons depend on the amount of eutectic carbides in the microstructure, and on the hardness of matrix (6, 7). The best wear resistance and the hardness possess the alloys with martensitic matrix. Alloys with martensitic-pearlitic matrix are softer, their hardness depends on the portion of pearlitic phase (11, 12).

The alloy for which the transformation diagrams were constructed exhibited as cast on the cross section cast in mould the average hardness 650 HV, and on the cross section cast into sand 635 HV respectively. Destabilized samples with martensitic matrix had hardnesses between 760 and 800 HV.

The highest hardness of alloys with 15 to 18 % Cr is obtained by hardening from the temperature between 940 and 970° C. For the alloys with higher contents of Cr (over 20 %) the temperatures of hardening are higher, up to 1010° C. Martensite is harder if more carbon is dissolved in austenite. Solubility of carbon increases with the increased temperature of hardening (18). By hardening from higher temperatures, also residual austenite can be obtained in the microstructure, especially if alloys contain over 1 % Mn. Also Ni (Cu) acts like Mn which on the other hand improves the through-hardenability. In our alloys the residual austenite was not detected by dilatometric investigations. The residual austenite was obtained in the matrix only under harsher conditions of hardening from higher temperatures.

The samples were hardened in air from the destabilization temperature of 970° C. Martensite is stable and the hardness starts to drop in tempering above 400° C **(Fig. 21)**. The hardness of alloys with sufficient portion of residual austenite increases in tempering between 450 and 550° C due to the decomposition of residual austenite into martensite. The transformation is connected with volume changes, and it is undesired because of internal stresses. Microstructural characteristics of tempered cast iron are shown in **Figs. 22 to 26**.

Zaostali avstenit lahko dobimo pri ostrejših pogojih kaljenja in pri višjih vsebnostih Mn in Ni.

Morfologija perlita je odvisna od stopnje destabilizacije, kot smo to že razložili pri izotermnih pogojih transformacije.
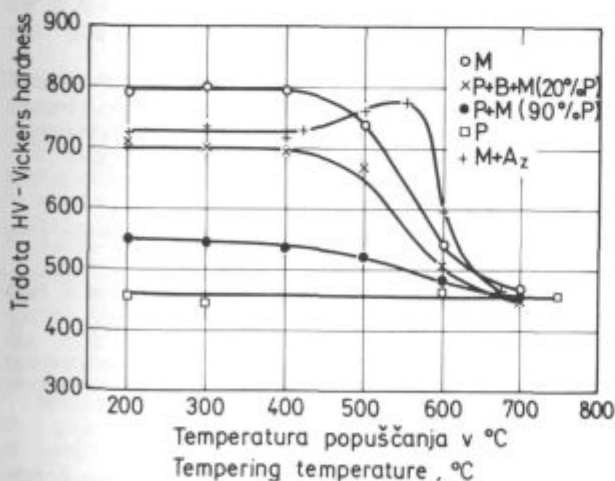
Trdota zlitin

Ustrezne uporabne lastnosti belih kromovih litin so odvisne od deleža evtektičnih karbidov v mikrostrukturi in trdote matice (6, 7). Najboljšo obrabno obstojnost in trdoto imajo zlitine z martenzitno matico. Zlitine z martenzitno perlitno matico so mehkejše, njihova trdota pa je odvisna od deleža perlitne faze. (11, 12).

Zlitina, za katero so narejeni transformacijski diagrami, ima v litem stanju na preseku ulitem v kokilo, povprečno trdoto 650 HV in na preseku ulitem v pesek 635 HV. Destabilizirani vzorci z martenzitno matico imajo trdoto med 760 in 800 HV.

Največjo trdoto zlitin s 15 do 18 % Cr dobimo pri kaljenju s temperature med 940 in 970 °C. Za zlitine z višjo vsebnostjo Cr (nad 20 %) so temperature kaljenja višje, do 1010 °C. Martenzit je trši, čim več C je raztopljenega v avstenitu. Topnost C narašča z naraščajočo temperaturo kaljenja (18). Pri kaljenju z višjih temperatur pa lahko dobimo v mikrostrukturi še zaostali avstenit, zlasti še, če vsebujejo zlitine nad 1 % Mn. Podobno kot Mn učinkuje tudi Ni (Cu), ki sicer izboljša prekaljivost. V naših zlitinah zaostalega avstenita z dilatometrskimi preiskavami nismo zasledili. Zaostali avstenit smo dobili v matici le pri ostrejših pogojih kaljenja z višjih temperatur.

Vzorce smo kalili na zraku s temperature destabilizacije 970 °C. Martenzit je stabilen in trdota prične padati pri popuščanju nad 400°C (**sl. 21**). Trdota zlitin z zadostnim deležem zaostalega avstenita pri popuščanju med 450 in 550 °C naraste zaradi razpada zaostalega avstenita v martenzit. Premena je povezana z volumskimi spremembami in je zaradi notranjih napetosti nezaželjena. Mikrostrukturne značilnosti popuščene litine so prikazane na **slikah 22, 23, 24, 25 in 26**.
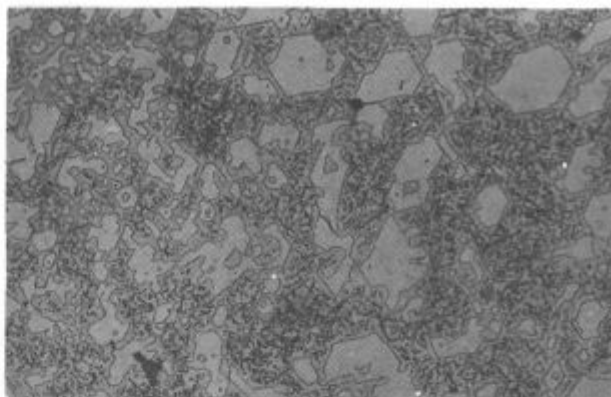

Sl. 22:
Mikrostruktura destabilizirane litine kaljene na zraku. Matica je iz sekundarnih karbidov in martenzita. Pov. 500 ×
Fig. 22
Microstructure of destabilized cast iron hardened in air. Matrix is of seconday carbides and martensite. Mag. 500 ×

Sl. 23:
Mikrostruktura kaljene litine 2 uri popuščane na 400°C. Pov. 500 ×
Fig. 23
Microstructure of hardened cast iron, tempered 2 hours at 400° C. Magn. 500 ×

Sl. 21:
Vpliv temperature popuščanja na trdoto destabilizirane litine z različno mikrostrukturo matice (M — martenzit, B — bainit, P — perlit, A$_z$ — zaostali avstenit)
Fig. 21
Influence of temperature of tempering on the hardness of destabilized cast iron with various microstructures of matrix (M — martensite, B — bainite, P — pearlite, A$_z$ — residual austenite)
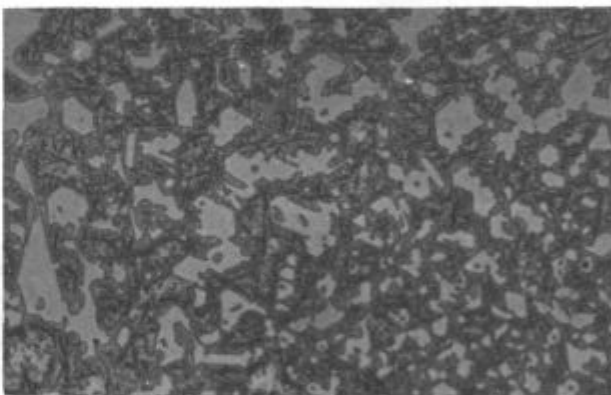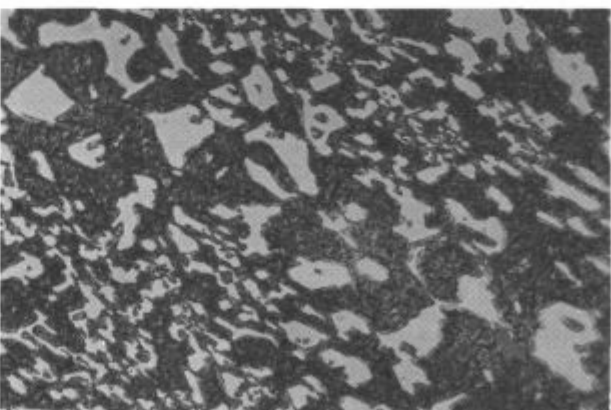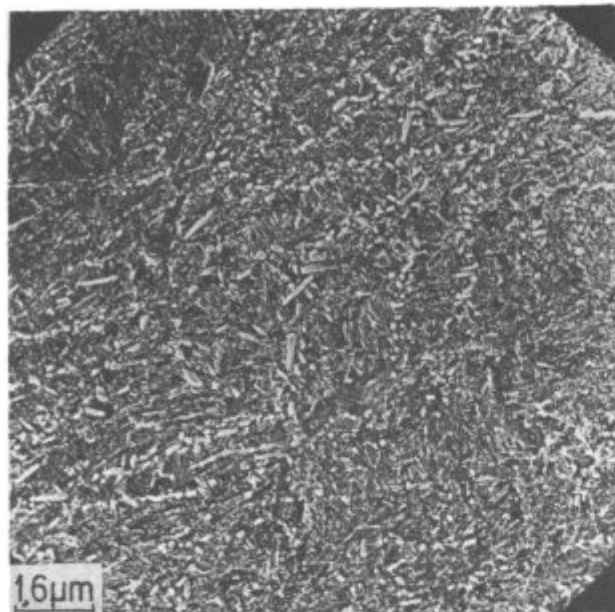

Sl. 24:
Mikrostruktura kaljene litine 2 uri popuščane na 600°C. Pov. 500 ×
Fig. 24
Microstructure of hardened cast iron, tempered 2 hours at 600° C. Magn. 500 ×

Sl. 25:
SEM posnetek na zraku kaljene litine. Mikrostruktura matice
je iz sekundarnih karbidov in martenzita.
Fig. 25
SEM picture of air-hardened cast iron. Microstructure of matrix
is of secondary carbides and martensite.

Sl. 26:
SEM posnetek kaljene litine 2 uri popuščane na 300°C
Fig. 26
SEM picture of hardened cast iron, tempered 2 hours at 300°C

S kontinuirnim ohlajanjem smo pripravili vzorce z
mešano perlitno-bainitno-martenzitno mikrostrukturo.
Potek trdote v odvisnosti od temperature popuščanja je
podoben kot pri vzorcih z martenzitno matico, le izhod-
na trdota je nižja. Trdota vzorcev s perlitno matico se
pri popuščanju ne spremeni.

Trdote ostalih preiskovanih zlitin z avstenitno mati-
co v litem stanju so podobne, tiste z avstenitno-perlitno
ali popolnoma perlitno matico pa so mehkejše in je nji-
hova trdota med 480 in 550 HV. Temu ustrezne so tudi
trdote po toplotni obdelavi. Trdota je pri zlitinah z av-
stenitno matico v litem stanju enaka po celem preseku
preizkusnih valjčkov.

Mikrotrdote posameznih mikrostrukturnih faz so
podane v **tabeli 4**. Pri karbidih M_7C_3 moramo upošteva-
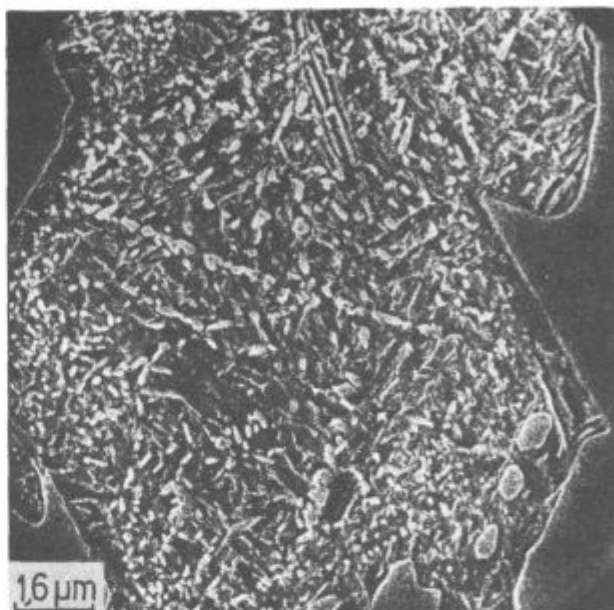ti, da je njihova trdota odvisna od kristalografske smeri,
v kateri jo merimo (6).

By continuous cooling the samples with mixed pearl-
itic-bainitic-martensitic microstructure were prepared.
The variation of hardness depending on the tempering
temperature is similar to that in the samples with mart-
ensitic matrix, only the initial hardness is lower.
Hardness of samples with pearlitic matrix does not
change in tempering.

Hardnesses of the other investigated as cast alloys
with austenitic matrix are similar to that of alloys with
austenitic-pearlitic matrix, but the alloys with fully pearli-
tic matrix are softer and their hardnesses varied be-
tween 480 and 550 HV. Similar relationship remains also
after the heat treatment. Hardness of the as cast alloys
with austenitic matrix is practically equal through the
whole cross section of testing cylinders.

Microhardnesses of single microstructural phases
are given in **Table 4**. It is necessary to take into account
that the hardness of M_7C_3 carbides depends on the crys-
tallographic direction in which it is measured (6).

Tabela 4: Mikrotrdote mikrostrukturnih faz   HV

Primarni in evtektički karbidi M_7C_3	900—1300
Martenzit, sekundarni karbidi	650—700
Avstenit	400—520
Perlit, sekundarni karbidi	360—420

Table 4 Microhardnesses of Microstructural Phases

Phase	HV
M_7C_3 primary and eutectic carbides	900 ... 1300
Martensite, secondary carbides	650 ... 700
Austenite	400 ... 520
Pearlite, secondary carbides	360 ... 420

ZAKLJUČEK

Opisane so nekatere mikrostrukturne značilnosti in
pogoji toplotne obdelave belih kromovih litin, legiranih
z Mo in z Ni, Si, Mn, V, Ti, in W, namenjenih za centri-
fugalno dvoslojno lite valje. Iz preiskav se vidi, da so
mehanske lastnosti odvisne od mikrostrukturnih značil-
nosti in s tem od kemične sestave, pogojev strjevanja in
ohlajanja ter toplotne obdelave.

Z ustreznim razmerjem Cr/C, legiranjem z Mo in
hitrim strjevanjem dobimo v litem stanju drobne evtek-

CONCLUSIONS

Some microstructural characteristics and the condi-
tions for heat treatment of white chromium cast irons al-
loyed with Mo, and with Ni, Si, Mn, V, Ti, and W which are
intended for centrifugal compound casting of rolls, are
presented in the paper. The investigations show that
mechanical properties depend on the microstructural
characteristics, and thus on the chemical composition,
conditions of solidification and cooling, and on the heat
treatment.

tične karbide in avstenitno matico, ki je s stališča nadaljnje toplotne obdelave najustreznejša. Sicer pa je matica lahko tudi avstenitno-perlitna ali perlitna.

Delež karbidne faze je odvisen predvsem od vsebnosti C. Primarni heksagonalni karbidi, ki nastajajo pri počasnem ohlajanju ali pri deležu karbidne faze, večjem od 35 %, so nezaželjeni, ker bistveno poslabšajo žilavost litin. Po kemični sestavi ustrezajo karbidi stehiometričnemu razmerju od $(Cr_3Fe_4) C_3$ do $(Cr_4Fe_3) C_3$. Z naraščajočo vrednostjo razmerja Cr/C narašča vsebnost Cr v karbidih. Karbidi M_7C_3 z več Cr so trši. V evtektičnih karbidih je pri istem razmerju Cr/C manj Cr kot v primarnih karbidih.

Trdota litin je odvisna od deleža evtektičnih karbidov in trdote mikrostrukture, ki jo dobimo po toplotni obdelavi. Osnova za toplotno obdelavo litin sta TTT diagrama za destabilizacijo avstenita in za destabiliziran avstenit in CTT diagram za destabiliziran avstenit.

Morfologija izločanja sekundarnih karbidov (destabilizacija avstenita) in perlitne transformacije nedestabiliziranega avstenita je podobna. Oba procesa potekata s kristalnih mej proti sredini kristalnih zrn, in to hitreje po določenih kristalografskih ravninah. V destabiliziranem avstenitu poteka kontinuirna perlitna transformacija.

Izločanje sekundarnih karbidov, ki poteka najhitreje med 940 in 990⁰ C, je bistvenega pomena za nadaljnjo toplotno obdelavo litin. Le v destabilizirani matici je mogoča martenzitna in tudi bainitna transformacija. Bainitna transformacija poteka počasi in je za prakso manj pomembna. Najtrše so litine z martenzitno matico. Z ustrezno toplotno obdelavo pa lahko dobimo zlitine z martenzitno-perlitno ali perlitno matico, ki so mehkejše. Pri popuščanju litin z martenzitno ali martenzitno-perlitno matico prične trdota padati pri temperaturah popuščanja nad 400 °C.

Suitable Cr/C ratio, alloying with Mo, and fast solidification enable the formation of fine eutectic carbides in the austenitic matrix in cast state which is the most desired from the viewpoint of further heat treatment. Matrix can also be austenitic-pearlitic or only pearlitic.

Portion of carbide phase depends mainly on the carbon content. Primary hexagonal carbides formed during slow cooling or in alloys containing more than 35 % of carbide phase are undesired since they essentially reduce the toughness of alloys. According to the chemical compositions the carbides correspond to stoichiometric ratios from $(Cr_3Fe_4)C_3$ to $(Cr_4Fe_3)C_3$. The increasing value of the Cr/C ratio causes the increased content of Cr in carbides. M_7C_3 with higher Cr content are harder. Eutectic carbides at the same Cr/C ratio contain less Cr than the primary ones.

Hardness of cast irons depend on the amount of eutectic carbides and on the hardness of the microstructure obtained by the heat treatment. Basis for the heat treatment of cast irons are the TTT diagrams for the destabilization of austenite, and for destabilized austenite, beside the CTT diagram for the destabilized austenite.

Morphologies of precipitation of secondary carbides (destabilization of austenite), and of pearlitic transformation of undestabilized austenite are similar. Both processes start on the crystal boundaries and proceed towards the centre of grains, and the process is faster along certain crystallographic planes. In destabilized austenite continuous pearlitic transformation takes place.

Precipitation of secondary carbides which is the fastest between 940 and 990° C is essential for further heat treatment of cast irons. Only in destabilized matrix the martensitic and also bainitic transformation is possible. Bainitic transformation is slow and it is less important for practical applications. The hardest are the alloys with martensitic matrix. By a suitable heat treatment the alloys with martensitic-pearlitic or pearlitic matrix can be obtained, but they are softer. In tempering the cast irons with martensitic or martensitic-pearlitic matrix, their hardness begins to decrease at the tempering temperatures above 400° C.

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