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**Effects of Carbon,  
Chromium and  
Molybdenum Contents  
on Solidification  
and Microstructure  
of 15 or 20% Cr  
White Cast Irons**

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Les effets des teneurs en carbone,  
chrome et molybdène sur la solidification  
et la microstructure des fontes blanches  
à 15 ou 20% Cr

Der Einfluss von Kohlenstoff-, Chrom-  
und Molybdängehalt auf die Erstarrung  
und das Mikrogefüge des weissen  
Gusseisens mit 15 oder 20% Cr-Gehalt

Влияние углерода, хрома и молибдена  
на затвердевание и микроструктуру  
отливок из белого чугуна с содержанием  
15 или 20% хрома

**Brasil**

## RÉSUMÉ

Des expériences ont été conduites sur les pièces d'épreuve à diamètre de 30 mm en fonte blanche à la teneur en chrome de 15 ou 20% et en carbone de 2,3; 3,0 et 3,6% avec d'additions de zéro, 1,5 ou 2,5% de molybdène pour chaque teneur en carbone.

Les mesures suivantes ont été prises: les arrêts de température d'austénite et d'eutectique; le nombre des particules de carbure d'eutectique par rapport au volume total et au volume eutectique; la fraction de volume d'austénite primaire.

Il était observé, que les teneurs en carbone élevées menaient à l'abaissement des arrêts de température de formation d'austénite et d'eutectique, à la réduction du nombre des particules de carbure dans le volume eutectique et à la réduction de la fraction de volume d'austénite primaire.

L'addition de molybdène menait à l'abaissement des arrêts de température de formation d'austénite et d'eutectique, à la réduction du nombre des particules de carbure dans le volume total et volume eutectique et à la croissance de la fraction de volume d'austénite primaire.

En comparaison avec les alliages à 15% Cr les alliages à 20% Cr montraient les arrêts de température d'eutectique plus élevés, plus de particules de carbure dans le volume total comme dans le volume eutectique et une plus petite fraction de volume d'austénite primaire.

## ABSTRACT

Solidification experiments were performed on 30 mm diameter test pieces of white irons containing 15 or 20% chromium and 2,3, 3,0 and 3,6% carbon, with additions of zero, 1,5 or 2,5% molybdenum for each carbon content.

Measurements were made of: austenite and eutectic temperature arrests; number of eutectic carbide particles relative to total volume and to eutectic volume; volume fraction of primary austenite.

It was observed that increasing carbon contents caused lower austenite and eutectic formation temperature arrests, reduced number of carbide particles in eutectic volume and smaller volume fraction of primary austenite.

The addition of molybdenum led to lower austenite and eutectic formation temperature arrests, less carbide particles in total and in eutectic volume, and larger volume fraction of primary austenite.

As compared to 15% chromium alloys, the 20% chromium alloys showed higher eutectic temperature arrests, more carbide particles both in the total volume and in the eutectic volume, and smaller volume fraction of primary austenite.

## ZUSAMMENFASSUNG

Es wurden Experimente durchgeführt mit der Erstarrung der 30-mm-Durchmesser-Probstücke aus weissem Gusseisen mit 15 oder 20% Cr-Gehalt und 2,3; 3,0 und 3,6 % C-Gehalt mit Zusätzen von 0; 1,5 und 2,5 % Molybdän bei jedem Kohlenstoffgehalt.

Folgendes wurde gemessen: austenitischer und eutektischer Temperaturstillstand; Anzahl der eutektischen Karbidpartikeln im Verhältnis zu dem Gesamtvolumen und dem eutektischen Volumen; Volumenanteil des primären Austenits.

Es wurde beobachtet, dass die Erhöhung des Kohlenstoffgehalts zum niedrigeren Temperaturstillstand der Austenit- und Eutektikumbildung, der Verminderung der Anzahl der Karbidpartikeln im eutektischen Volumen und dem kleineren Volumenanteil des primären Austenits führte.

Der Zusatz von Molybdän führte zum niedrigeren Temperaturstillstand der Austenit- und Eutektikumbildung, der Verminderung der Anzahl der Karbidpartikeln im Gesamt- und eutektischen Volumen und dem grösseren Volumenanteil des primären Austenits.

Im Vergleich zu 15%-Cr-Legierungen zeigten die 20%-Cr-Legierungen höhere eutektische Temperaturstillstände, mehr Karbidpartikeln sowohl im Gesamt- als auch im eutektischen Volumen und einen kleineren Volumenanteil des primären Austenits.

## РЕЗЮМЕ

Проводились эксперименты по затвердеванию образцов диаметром 30 мм из белого чугуна, содержащего 15 или 20% хрома и 2,3; 3,0 и 3,6 % углерода с добавками 0; 1,5; 2,5% молибдена соответственно содержанию углерода.

Производились измерения: температуры превращения аустенита и эвтектики; количества эвтектических карбидных частиц относительно общего объема и объема эвтектики; объемной доли первичного аустенита.

Наблюдения показали, что повышение содержания углерода приводило к снижению уровня температуры аустенитного превращения и эвтектики, уменьшению количества карбидных частиц в объеме эвтектики и уменьшению объемной доли первичного аустенита.

Добавка молибдена приводила к снижению температуры аустенитного превращения эвтектики, уменьшению количества карбидных частиц в общем объеме и объеме эвтектики и увеличению объемной доли первичного аустенита.

По сравнению со сплавами с 15 % хрома сплавы с 20 % хрома обнаружили более высокую температуру эвтектики, большее количество карбидных частиц как в общем объеме, так и в объеме эвтектики и меньшую объемную долю первичного аустенита.

# Effects of Carbon, Chromium and Molybdenum Contents on Solidification and Microstructure of 15 or 20% Cr White Cast Irons

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## 1. INTRODUCTION

The solidification sequence and microstructure of high chromium white cast irons are dependent on chemical composition. Chromium and carbon contents are factors which determine the actual amount of primary austenite on solidification, as well as the nature of the eutectic carbide formed ( $M_3C$  or  $M_7C_3$ ).

According to Maratray and Nanot (1) the amount of primary austenite formed at the solidification determines the microstructure of the eutectic. For these authors, if the volume fraction of primary austenite is large, then the carbide tends to «segregate» along the grain boundaries. Should the volumetric fraction of carbides reach as much as 20 or 30 %, then the morphology of the eutectic could be described as eutectic cells or colonies. A third kind of morphology is described by Maratray for alloys whose austenite does not regulate eutectic formation, as occurs in alloys with near-eutectic compositions. These are said to exhibit lamellar structures (1).

By removing the austenite with a deep etch, Powell (2) was able to observe the eutectic carbide structures in a scanning electron microscope. The carbide was

shown to be interconnected within each eutectic cell, intermingling with austenite, much in the same way as silicon appears in the eutectic of modified Al—Si alloys.

Matsubara (3) found out that to a rise in chromium content from 15 to 30 % corresponded a decrease in eutectic cell diameter and, at the same time, smaller inter-carbide spacings at the edge of the eutectic cell. These two effects were ascribed to the reduction of the eutectic solidification range.

Although the effect of carbon is not discussed by Matsubara (3) it may be inferred from his experimental results that higher carbon contents promote the enlargement of both the eutectic colonies diameter and the inter-carbides spacing at cell edge.

Other authors found out that the larger the cooling rate, the finer the eutectic morphology (4).

Three different approaches to the study of these materials can be identified in the technical literature, each one considering part of the phenomena which are influential on eutectic morphology. One of these approaches, due to Maratray and Nanot (1), is based on the partition of space during solidification. From this point of view the austenite volume being small or large, conditions the extension of the growth of eutectic aggregate. Another approach attributes eutectic shape changes to alloy chemistry differences, particularly explaining  $M_7C_3$  eutectic refinement as an effect of chromium content variation (3). Finally the refinement of eutectic structure is associated with faster cooling rates (4).

Molybdenum has been extensively employed as alloying element in high chromium white cast irons mainly in order to enhance hardenability without substantial rising of the temperature of start of martensite formation thus avoiding larger amounts of retained austenite after quench. This accounts for many research works which have been carried out on the effect of molybdenum on heat treating, whereas only scarce studies are to be found in literature dealing with molybdenum effect on solidification microstructure of Fe—Cr—C alloys.

Jellinghaus (5), in one of the few studies ever carried out on the effects of chromium and molybdenum on the solidification structure, found that the joint

addition of these two elements to Fe-Cr-C alloys brought about a decrease of the liquidus surface temperature. Also, he concluded that the carbides could be either  $Mo_2C$  or  $M_6C$  according to the prevalent % Cr/% C relationship and to the molybdenum content of the alloy.

## 2. EXPERIMENTAL MATERIALS AND METHODS

Starting with two base alloys containing 15% or 20% chromium and 2.3% carbon, several remelting operations were conducted in order to obtain eighteen chemical compositions corresponding to eutectic and hypoeutectic alloys. The final analyses showed Cr and Mo contents very close to the aimed ones, whereas actual carbon contents obtained are shown in Table I.

Table I  
Carbon contents, austenite and eutectic temperature arrests

Alloys Cr-C-Mo	C, %	$T_V$ , °C	$T_E$ , °C
15-2.3-0	2.25	1321	1253
15-3.0-0	2.94	1281	1238
15-3.6-0	3.52	—	1229
15-2.3-1.5	2.21	1246	1317
15-2.3-2.5	2.24	1240	1308
15-3.0-1.5	2.94	1232	1281
15-3.0-2.5	2.99	1227	1281
15-3.6-1.5	3.43	1224	1224
15-3.6-2.5	3.65	1217	1217
20-2.3-0	2.24	1331	1263
20-3.0-0	2.95	1285	1254
20-3.6-0	3.44	—	1244
20-2.3-1.5	2.20	1250	ND
20-2.3-2.5	2.20	1243	1321
20-3.0-1.5	3.01	1242	1266
20-3.0-2.5	3.09	1238	1263
20-3.6-1.5	3.44	1235	1235
20-3.6-2.5	3.55	1230	1230

Cylindrical test pieces were obtained by pouring the molten alloys into regular shell sand cups for thermal analysis, having 30 mm internal diameter and about 50 mm height, fitted with an axially positioned chromel-alumel thermocouple.

The metal was poured directly from the silicon carbide crucible into the thermal analysis cups. This practice allowed adequate pouring temperature control, which

was kept between 1450 and 1460°C for 15% Cr alloys and 1480 and 1500°C for 20% Cr alloys.

Metallographic samples were taken from transverse slices cut from the cylindrical test pieces at a location immediately above the thermocouple tip so as to assure correlation between microstructure and thermal analysis.

The volumetric fractions of constituents were determined using a 25 point grid, by making 30 counts per sample, according to ASTM-E-562-76 standard.

Carbide particles were counted with the aid of a 0.314 mm perimeter circle and expressed as counts per unit length of line.

## 3. RESULTS AND DISCUSSION

### 3.1. 15% Chromium alloys containing zero, 1.5 and 2.5% molybdenum

As a general rule, the results obtained in the experiments performed with all the 15% chromium alloys, regardless of molybdenum content, were similarly affected by carbon content: as carbon content was increased, austenite and eutectic temperature arrests decreased, whereas increased carbide volume fractions and carbide particles numbers were detected in both eutectic and total volumes.

#### Thermal analysis.

Table I presents the austenite and eutectic temperature arrests as affected by carbon content, for zero, 1.5 and 2.5% molybdenum alloys. The same results are also shown in fig. 1. Austenite temperature arrest exhibits a marked decrease as the eutectic composition is approached. The proximity of eutectic composition may be appraised from fig. 2.

These results show that higher carbon contents provoke also a decrease of the eutectic reaction temperature. The fact that different solidification paths are followed in each case as shown in fig. 2, affords an explanation for this effect. In fact, as fig. 2 shows schematically, the higher the carbon content, the lower the temperature at which the eutectic monovariant line  $U_1-c_1$  is reached.

As compared to zero molybdenum condition, additions of 1.5 or 2.5% Mo lead to small but significant decrease in austenite temperature arrest for the 2.3% C alloy. No effect of this kind is observed for 3% C alloy probably as a result of

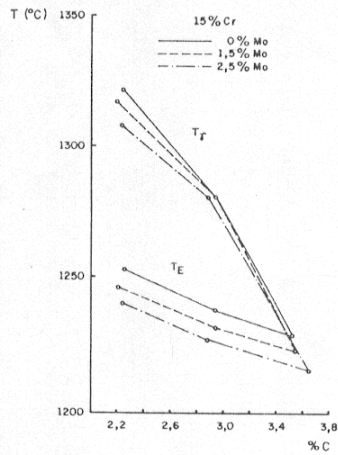


Fig. 1. Austenite temperature and eutectic temperature

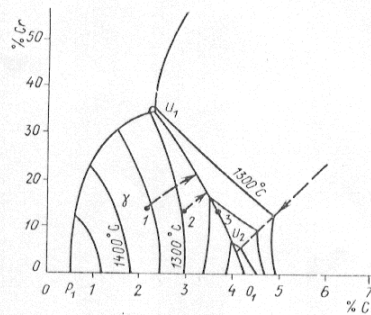


Fig. 2. Liguidus surface of Fe—Cr—C phase diagram. Schematic solidification paths for alloys with 15% Cr—2.3(1); 2.9(2) and 3.6% C

the strong influence which small variations of both the carbon content and the cooling rate exert on austenite temperature arrest ( $T_a$ ).

Similar difficulties were met with 20% chromium alloys, although decreases in austenite temperature arrests with molybdenum additions are reported by Kirkaldy (6) for steels and by Jellinghaus (5) for Fe—Cr—C—Mo alloys.

It may be clearly noticed in fig. 1 a progressive reduction of eutectic temperature arrest as molybdenum additions

are made at same carbon level. Quite similar results were obtained by Matsubara (7): by adding Mo to 15 and 30% chromium alloys, he detected lower temperatures of start and end of eutectic solidification.

It can thus be stated that molybdenum additions up to 2.5% alters the solidification path of the austenite, changing the Fe—Cr—C ternary phase diagram, though not severely restraining its use as a technological tool for the interpretation of solidification process in commercial alloys.

#### Quantitative metallography: Austenite volume fraction ( $V_a$ ) and Carbide volume fraction ( $V_k$ ).

Table 2 and fig. 3 show that, for molybdenum free alloys (solid lines in fig. 3),  $V_a$  diminishes as the carbon content is increased.

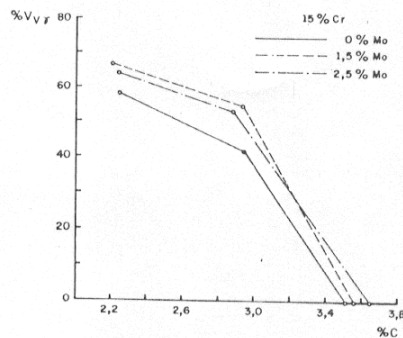


Fig. 3. Volume fraction of primary austenite  $V_a$ , as a function of carbon content

This fact is too explained by the closer proximity of higher carbon alloys to the eutectic line. The observed decrease of  $V_a$  is much more marked for the 3.0 to 3.6% C change than for the 2.3 to 3.0% C change.

Fig. 3 shows also that the addition of molybdenum entailed an increase in austenite volume fraction, but no significant change of  $V_a$  can be detected when molybdenum addition is raised from 1.5 to 2.5%. These observations suggest the occurrence of changes in the solidification paths when molybdenum is added.

Table 2  
Volume fraction of austenite and volume fraction of carbide

Alloys Cr-C-Mo	$V_{V_A}, \%$	$V_{V_K}, \%$
15-2,3-0	58,7±3,1	16,1±2,7
15-3,0-0	41,7±3,3	25,2±3,4
15-3,6-0	0	28,6±3,5
15-2,3-1,5	65,6±3,2	17,0±2,5
15-2,3-2,5	64,1±4,1	14,8±1,6
15-3,0-1,5	54,4±3,5	25,4±2,5
15-3,0-2,5	53,1±2,8	23,6±2,5
15-3,6-1,5	0	25,5±2,9
15-3,6-2,5	0	31,3±3,3
20-2,3-0	56,0±2,6	15,6±2,7
20-3,0-0	33,1±3,2	24,7±2,8
20-3,6-0	0	32,3±3,5
20-2,3-1,5	61,9±4,2	19,9±2,0
20-2,3-2,5	59,1±3,5	18,4±3,2
20-3,0-1,5	35,4±3,1	26,0±2,3
20-3,0-2,5	38,0±3,5	25,3±3,1
20-3,6-1,5	0	32,5±3,0
20-3,6-2,5	0	31,1±3,4

so that the eutectic line would be reached only when a lesser quantity of liquid would remain for the eutectic solidification. Apparently, though, some mechanism limits this austenite promoting effect of molybdenum.

As stated in the literature (1,8), the carbide volume fraction  $V_{V_K}$  increases as carbon content is increased, but molybdenum apparently does not influence  $V_{V_K}$ ; the same conclusion can be drawn by computing data from Maratray (1) and Zum-Gahr (8).

**Quantitative metallography:** Carbide particle number per line length in the total volume and in the eutectic volume.

As shown in Table 3 and fig. 4, the carbide particle count in total volume ( $N_{T_i}$ ) increases with carbon content up to eutectic composition, both in alloys with and without molybdenum. This feature was predictable since it is a direct consequence of the decrease of  $V_{V_A}$  as the composition comes nearer the eutectic line.

In order to ascertain the effects of carbon and molybdenum on the solidification structures of the eutectic microconstituents independently of the austenite volume fraction, the number or carbide particles per unit length of line in the eutectic region was computed as

$$N_{E_i} = N_{T_i}(1 - V_{V_A}),$$

Table 3  
Eutectic carbide particle number in total volume ( $N_{T_i}$ ) and in eutectic volume ( $N_{E_i}$ )

Alloys Cr-C-Mo	$N_{T_i}$	$N_{E_i}$
15-2,3-0	75,1±7,5	181,7±11,1
	82,2±6,9	141,3±9,4
	84,6±6,5	84,6±6,5
15-3,0-0	48,8±4,6	141,7±9,6
15-3,6-0	50,6±7,2	140,9±9,4
15-3,0-1,5	59,6±5,5	130,8±8,9
15-3,0-2,5	64,3±5,3	237,7±8,3
15-3,6-1,5	67,4±4,7	67,4±4,7
15-3,6-2,5	80,1±7,9	80,1±7,9
20-2,3-0	90,0±8,9	195,7±12,3
20-3,0-0	97,8±7,1	146,1±9,4
20-3,6-0	82,5±6,8	92,5±6,8
20-2,3-1,5	63,8±6,3	165,0±9,5
20-2,3-2,5	64,5±5,5	157,0±9,7
20-3,0-1,5	77,8±5,3	131,4±6,6
20-3,0-2,5	71,6±6,0	115,5±8,3
20-3,6-1,5	74,5±5,5	74,5±5,5
20-3,6-2,5	79,5±5,6	79,5±5,6

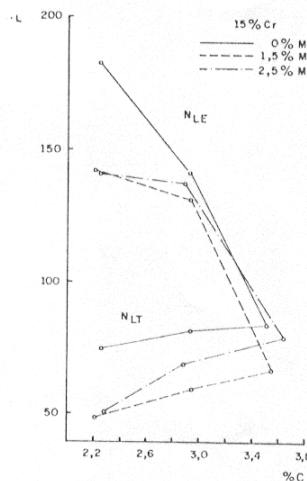


Fig. 4.—Eutectic particle number in total volume ( $N_{T_i}$ ) and in eutectic volume ( $N_{E_i}$ ) as a function of carbon content

i. e., those parts of the line crossing the austenite region are subtracted from the total line length.

When plotted against % Carbon, fig. 4,  $N_{E_i}$  calculated values exhibit a very pronounced decrease which, together with the concurrent decrease of  $V_{V_A}$ , reflect

a coarsening of the eutectic carbides. An analogous behaviour is encountered among grey cast irons where the very branched undercooled graphite morphologies (types D and E) give way to the coarser A type when carbon equivalent approaches the eutectic value, other factors as bath condition and cooling rate kept unchanged.

Two factors may be considered to influence the refining of eutectic carbides. The first one relates to the partition of space among the austenite dendrites and the eutectic: the more hypoeutectic the alloy, the less will be the volume of liquid remaining for eutectic solidification, giving smaller eutectic cells. The second factor is a chemical one: the more hypoeutectic the alloy, the higher will be both the eutectic arrest and the chromium content of the liquid at the eutectic freezing, as may be seen in fig. 2. This could cause carbide refining since, according to Matsubara (7), the higher the chromium content of eutectic alloys, the finer will be the carbides and the shorter will be the solidification range.

A microstructural analysis reveals: lengthier carbides as carbon content is raised from 2.3 to 3.0 %;

thicker carbides at increasing distances from eutectic cell centers; this coarsening is more marked for the 3.0 % C alloy than for the 2.3 % one;

more hexagonal and coarse carbides at eutectic cell edge for the higher carbon contents; these carbides are the bulkiest in the eutectic alloy.

The foregoing remarks are schematically represented in fig. 5.

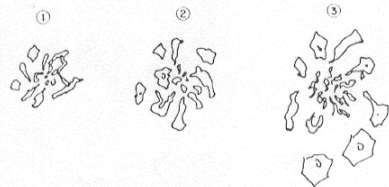


Fig. 5. Morphology of eutectic cell forms increasing carbon contents (1) 2.3%; (2) 2.9% and (3) 3.6% C

The increasing inter-carbide spacings as the eutectic cell boundary is approached can be explained making reference to the solidification sequence of a eutectic alloy. Solidification starts with nu-

cleation of eutectic colonies; as the eutectic cells become larger, the temperature and the composition follow the eutectic line from  $U_1$  to  $e_1$  (fig. 2). In other words, the eutectic solidification would take place at decreasing temperatures if equilibrium were to be attained. However, the solidification actually takes place, at least partially, at a constant temperature (the eutectic arrest). Therefore the actual solidification process occurs at gradually smaller undercoolings as eutectic solidification proceeds, as represented in fig. 6. Smaller undercoolings

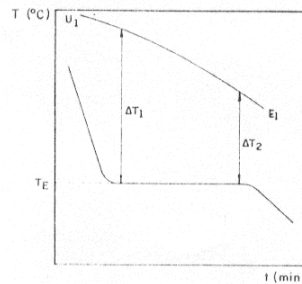


Fig. 6. Undercooling changes during eutectic solidification

reduce the carbide branching frequency and, consequently inter-particle spacings are increased as the eutectic cell boundary advances. Another possible explanation for the observed increase in carbide particle spacings might be the solute gathering at liquid eutectic cell interface, thus changing constitutional undercooling.

The carbide thickening and the presence of hexagonal carbides at cell boundaries admit a similar explanation. At the start of eutectic freezing, when higher undercoolings prevail, the driving force is large enough to support the high branching frequency and the creation of interfaces between austenite and carbide at the eutectic cell. Both carbide and austenite adopt then the morphology which is adequate for fast growth. Afterwards, at lower undercoolings, the driving force is less intense, causing the carbides to change their shape in order to spend less surface energy. An evidence which corroborates this explanation is the presence at cell boundaries of



carbides having hexagonal cross-section, which is the equilibrium form of  $Cr_7C_3$ .

Additions of molybdenum cause the carbide particle counts both in the total volume and in the eutectic volume to decrease, and the carbides to coarsen, confirming the observations made by Matsubara for eutectic alloys (7). This could be attributed to molybdenum segregation out of the eutectic cell.

No clear difference between carbide particle counts is noted for the two different molybdenum additions (1,5 and 2,5 % Mo), suggesting the existence of some sort of limit for this effect of molybdenum, much in the same line of what was said above in relation to the austenite volume fraction. This limiting mechanism will recur in 20 % chromium alloys, so that, within the limits of these experiments,  $V_{v_a}$ ,  $N_{c_1}$  and  $N_{t_1}$  are sensitive to molybdenum presence but apparently insensitive to its actual content.

The widening of inter-carbide spacings as a result of molybdenum addition has been attributed by Matsubara and co-workers (7) to an enlargement of the eutectic freezing range caused by this element. This effect is probably related to the segregation of molybdenum to the liquid during freezing.

### 3.2. 15—20% chromium alloys

The manner in which carbon and molybdenum affect the variables measured is the same for 20 % chromium as for 15 % chromium alloys. As carbon content is increased, austenite and eutectic arrests become progressively lower,  $V_{v_a}$  and  $N_{c_1}$  decrease, while  $V_{v_k}$  increases. The effects of adding molybdenum to 20 % chromium alloys are also very similar to those observed for 15 % chromium alloys.

When the characteristics of 20 % chromium alloys are compared to those obtained in 15 % chromium alloys, the following general observations are evident:

15 % chromium alloys present lower austenite and eutectic arrests;

at any given carbon content,  $V_{v_a}$  is smaller for 20 % chromium alloys because these are nearer the eutectic monovariant line.

$N_{t_1}$  and  $N_{e_1}$  are larger for 20 % chro-

mium alloys as consequences of the smaller austenite volume fraction and of the shorter eutectic freezing range.

## 4. SUMMARY

Fig. 7, 8, and 9 summarize the combined effects of carbon, chromium and molybdenum observed. The results for 2,5 % Mo addition are omitted in fig. 8, 9, because they do not differ significantly from those obtained with 1,5 % Mo addition.

Fig. 7 shows how chemical composition influences austenite and eutectic formation temperature arrests ( $T_a$  measurements relative to 1,5 % Mo additions do not show up in fig. 7). It may be

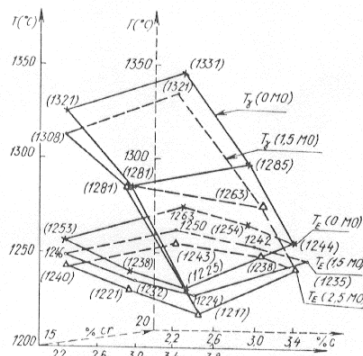


Fig. 7. Effect of Cr, C, and Mo on austenite and eutectic temperature ( $T_a$  and  $T_e$ )

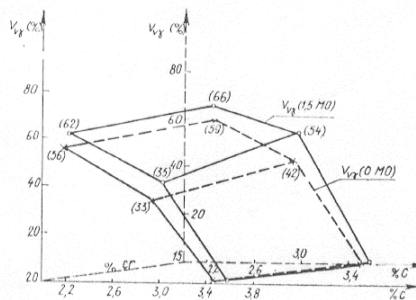


Fig. 8. Effect of Cr, C and Mo on austenite volume fraction ( $V_{v_a}$ )

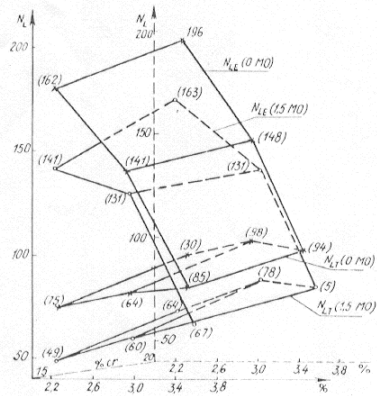


Fig. 9. Effect of Cr, C and Mo on carbide particle number in total volume ( $N_{c1}$ ) and in eutectic volume ( $N_{c1}$ )

clearly seen how carbon and molybdenum lower the eutectic arrest, while chromium raises it.

Fig. 8 shows how the austenite volume fraction is decreased by increasing carbon and/or chromium contents, and/or suppressing molybdenum.

Finally, fig. 9 depicts the influence of chemical composition on the number of carbide particles.

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