The Mo-C system has been studied by many authors. A list of references to these investigations, together with a portion of the Mo-C phase diagram, plotted from data obtained in [2, 3], is given in [1]. This diagram is based on the existence of the congruently melting molybdenum carbide MoC, which forms a eutectic with carbon at about 70 at. % C and a temperature of 2400°C. However, recent studies, whose results are summarized in [4], uniquely demonstrate that the composition of the carbon-rich molybdenum carbide is given by the formula Mo₂C₂.

This carbide exists in two modifications: α-cubic, of the B₁ (NaCl) type, space group O₄, and η-hexagonal, of the Ag (graphite) type, space group D₆₄h. The α ↔ η transformation temperature is of the order of 2200°C. At a temperature of about 1800°C, the η-phase decomposes:

\[ \eta \rightarrow \gamma + C, \]

where γ is the hexagonal molybdenum carbide Mo₂C₂(D₆₄h).

Since the recent data concerning the phases existing in the system Mo-C introduce many changes into the Mo-C phase diagram, it was considered of interest to modify the carbon-rich part of this diagram.

For the investigation, Mo-C alloys in the composition range between 20 and 50 at. % C (at intervals of 2 at. % C) were prepared by arc melting. They were annealed near the solidus temperature, and were subjected to metallographic and x-ray diffraction examinations. In addition, the initial melting points were measured by the Altermium-Pirani method. The results of the solidus temperature measurements were verified by metallographic analysis.

The results obtained lead to the following conclusions. Both the Mo₂C and Mo₂C₂ carbides exist in the composition range investigated. The MoC carbide was not detected. The existence of the eutectic reaction \[ L \rightarrow MoC + C \] at a temperature of about 2400°C was not confirmed.

Beginning from 40 at. % C, all alloys melt at the same temperature, viz., 2560 ± 20°C. In the structure of as-cast specimens containing not less than 40 at. % C, differently oriented, coarse precipitated particles of graphite produced by primary crystallization are observed; the amount of this graphite steadily increases with increasing carbon content of the alloys.

It was found possible substantially to superheat specimens containing 40, 48, and 50 at. % C above the solidus (Δt up to 150°C), without fully melting them. All this evidence points to the formation of the molybdenum carbide Mo₂C₂ at a temperature of 2560 ± 20°C according to the peritectic reaction:

\[ 3Mo + 2C \rightarrow Mo₂C₂ + Mo. \]
Fig. 3. Mo-C phase diagram plotted from data in [2] and [3].

$$L_1 + C \rightleftharpoons Mo_3C_2.$$ A comparison of the results obtained in the microstructural examination and the measurements of the initial melting point leads to the conclusion that a small region of homogeneity of the Mo$_3$C$_2$ phase exists at temperature close to the solidus temperature.

The molybdenum carbide Mo$_3$C is formed by the peritectic reaction:

$$L_3 + Mo_3C_2 \rightleftharpoons Mo_2C$$

at a temperature of 2425 ± 20°C, which is in good agreement with literature data. Naturally, the solubility of molybdenum in Mo$_3$C markedly changes with increasing temperature near the eutectic temperature.

Figure 1 shows the phase diagram of the system Mo-C, constructed from our data and those taken from [4]. The experimental points obtained in this investigation have been plotted on this diagram. Figure 2 shows characteristic microstructures of alloys with 40 and 50 at. % C, and, for comparison, the microstructure of a cast alloy with 50 at. % C, 20 at. % Mo, and 30 at. % Ti, whose structure exhibits a graphite-containing eutectic.

In Fig. 2a, the decomposition structure of the carbide Mo$_3$C$_2$ can clearly be seen. Since, according to [4], the cubic molybdenum carbide Mo$_3$C$_2$ forming during solidification undergoes during cooling two transformations ($\alpha \rightleftharpoons \eta$ and $\eta \rightleftharpoons \gamma + C$), which take place at high rates, it is impossible to decide on the basis of our data which process is responsible for this structure. It can only be pointed out that the strongest lines in the diffraction pictures of the first two alloys, obtained in CuK$_\alpha$ radiation (URS-501 X-ray apparatus), coincide with those cited in [3] and [6] for MoC; in accordance with [4], these correspond to the hexagonal modification $\eta$-Mo$_3$C$_2$.

The claim concerning the peritectic character of Mo$_3$C$_2$ crystallization and the absence of a eutectic at about 70 at. % C agrees with observations made in [5] and [7]. However, the results of melting point determination, made in [3] for six alloys with more than 33.5 at. % C and used for plotting the corresponding part of the phase diagram, are not reliable, since conclusions regarding the presence of eutectic transformation in this part of the diagram cannot be arrived at without microstructural examination.