In searches for new high-temperature materials, it should prove particularly advantageous to explore systems composed of transition metals and nonmetals, since alloys belonging to such systems possess high heat, oxidation, and wear resistance and many other attractive properties. The work described below was devoted to a study of the system Mo–W–C.

Binary Systems. In the binary systems Mo–C [1, 2] and W–C [3-5], there exist, according to recent data, the monocarbides \( \alpha\)-MeC\(_{1-x}\) with the cubic NaCl structure and the semicarbides \( \beta\)-Me\(_2\)C with the hexagonal NiAs structure, which, on cooling, becomes transformed into the ordered orthorhombic \( \xi\)-Fe\(_2\)N modification. In addition to the compounds mentioned above, the monocarbide \( \eta\)-MoC\(_{1-x}\) and the carbide WC are known to form in the systems molybdenum–carbon and tungsten–carbon, respectively; these carbides have their own distinctive hexagonal structures. The compounds \( \alpha\)-WC\(_{1-x}\), \( \alpha\)-MoC\(_{1-x}\), \( \eta\)-MoC\(_{1-x}\), and W\(_2\)C decompose eutectoidally at temperatures of 2530, 1960, 1655, and 1250°C, respectively. In the system Mo–W, the components have been found to exhibit unlimited solubility for each other [6].

System Mo–W–C. The phase equilibria in this system were first studied by Albert and Norton [7], who constructed, on the basis of x-ray diffraction analyses of a small number of alloys, a schematic isothermal section of the constitution diagram of the system at 1710°C.

Later, the system was studied in detail at 2200 and 2000°C by the methods of x-ray diffraction, metallography, and microhardness measurement, and isothermal sections at these temperatures were plotted for compositions with up to 50 at. % C [8]. In that work, the existence was established of limited solid solutions based on the carbides \( \alpha\)-MoC\(_{1-x}\), \( \eta\)-MoC\(_{1-x}\), and WC and of a continuous series of solid solutions between Mo\(_2\)C and W\(_2\)C. At these two temperatures and also at 1500°C, a hexagonal form of the carbide \((\text{Mo, W})_2\)C was observed; when quenching was performed at a cooling rate of not more than 20–30°C/sec, an orthorhombic modification was found to appear in the alloys investigated.

According to Rudy and Windisch [5], ordered orthorhombic modifications of W\(_2\)C and Mo\(_2\)C form a continuous series of solid solutions, the temperature of the order–disorder reaction changing continuous from 1430 (Mo\(_2\)C) to 2100°C (W\(_2\)C).

In a study of the solubility of carbon in the Mo–W solid solution, the present authors demonstrated that the width of the homogeneity range of the ternary (Mo, W, C) solid solution at 2000°C steadily decreases in the direction from the Mo–C side (0.6 at. % C) to the W–C side (0.2–0.1 at. % C). At 1000°C, the boundary lies between 0.1 and 0.05 at. % C at the molybdenum end and outside the sensitivity limits of chemical analysis for carbon at the tungsten end [9].

The aim of the present work was to study the phase equilibria in the system Mo–W–C at 1000°C. Alloy specimens were prepared and investigated by techniques similar to those described in [8]. The heat treatment of the specimens consisted of stepwise annealing operations carried out at 2200, 2000, and 1500°C in a vacuum furnace and at 1000°C in a silit-rod furnace, using evacuated quartz capsules. The duration of annealing varied, depending on the alloy composition, from 3 to 48 h at the high temperatures and from 400 to 700 h at 1000°C. In a few cases, the annealing of specimens at 1000°C was performed for 3000 h. After the heat treatment, the specimens were quenched in ice water. All the alloys were subjected to chemical analysis.

The data yielded by x-ray diffraction studies and metallographic examinations of quenched specimens were used to construct an isothermal section of the Mo–W–C constitution diagram at 1000°C for composi-
tions with up to 50 at. % C (Fig. 1). At this temperature, the carbides \( \alpha\)-MoC\(_{1-x}\) and \( \eta\)-MoC\(_{1-x}\) are absent and free carbon is in equilibrium with a WC base solid solution and a \((\text{Mo}, \text{W})\)\(_2\)C solid solution containing up to 3 at. % W. The carbon homogeneity range of \((\text{Mo}, \text{W})\)\(_2\)C is less than 2 at. % wide. Its upper limit passes below 33 at. % C, while its lower limit lies above 31 at. % C.

After annealing for 400 h at 1000°C, x-ray diffraction pictures of all the alloys exhibited a broadening of some lines, pointing to an ordering of carbon atoms and a lowering of the structural symmetry of \((\text{Mo}, \text{W})\)\(_2\)C from hexagonal to orthorhombic. The line broadening effect became more pronounced with increase in annealing time. Annealing for 1500 h was found to lead not only to the formation of the orthorhombic modification but also the eutectoid decomposition of the continuous series of \((\text{Mo}, \text{W})\)\(_2\)C solid solutions on the tungsten-rich side (at up to 10 at. % Mo) into \((\text{W}, \text{Mo})\)C and \((\text{W}, \text{Mo}, \text{C})\) solid solutions. The rate of the decomposition was very low: analysis of \((\text{W}, \text{Mo})\)\(_2\)C alloys held at that temperature for 3000 h revealed that the decomposition had been less than half completed in that time. In [10], annealing for 1500 h at 1000°C was sufficient fully to decompose \((\text{W}, \text{Mo})\)\(_2\)C and \((\text{Mo}, \text{W})\)\(_2\)C depends on the conditions of preparation and heat treatment of alloys.

To determine the temperatures of the ordering reaction, a few alloys containing 32.4-34.5 at. % C and up to 10.2 at. % W were subjected in our work to thermal analysis. As a result, thermal effects characteristic of solid-state transformation were observed at temperatures of 1300°C for Mo–6.6 at. % W–32.4 at. % and Mo–6.6 at. % W–33.4 at. % C alloys and 1325°C for a Mo–10.2 at. % W–34.5 at. % C alloy (Fig. 2) during heating. After thermal analysis, the specimens were annealed at 1300°C, quenched from that temperature, and then studied by x-ray diffraction. The diffraction pictures obtained were found to exhibit an orthorhombic splitting of lines. As noted above, after quenching from 1500°C all alloys from the Mo\(_2\)C–W\(_2\)C section had the hexagonal structure. Our results indicate that Rudy and Windisch's conclusion [5] concerning the ordering temperature of the \((\text{Mo}, \text{W})\)\(_2\)C solid solution requires confirmation.

**LITERATURE CITED**