Neutron diffraction study of the Ti$_{1-x}$Mo$_x$C alloy

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Abstract. In this work, the crystal structure and (RMSD) root-mean-square displacement of atoms in new cubic refractory interstitial alloys Ti$_{0.74}$Mo$_{0.26}$C and Ti$_{0.70}$Mo$_{0.30}$C were determined by neutron diffraction. These alloys are obtained by powder metallurgy by sintering fine powders of cubic titanium carbides TiC and molybdenum MoC. The values of the RMSD of atoms in these alloys, obtained by the methods of least squares and full-profile analysis from the neutron diffraction data, turned out to be identical. They turned out to be much larger than in the stoichiometric TiC alloy, which has a similar cubic structure and close geometric parameters of atoms with the Ti$_{0.74}$Mo$_{0.26}$C and Ti$_{0.70}$Mo$_{0.30}$C alloys. These alloys were explained by the occurrence of large static distortions in the lattice of the Ti$_{0.70}$Mo$_{0.30}$C alloy due to the differences in the masses and atomic radii of the titanium and molybdenum elements.

1. Introduction

Recently, due to the acute shortage of tungsten, it was necessary to find alloys that replace tungsten-containing alloys. One of such alloys can be alloys of Ti-Mo-C system [1-3]. A number of works are devoted in order to obtain and study the properties of single-phase alloys of Ti-Mo-C system [4-9]. However, obtaining single-phase alloys of the Ti-Mo-C system with large Mo content is apparently difficult because of the sharp difference in the thermodynamic parameters of the components [7, 8].

If until now a single-phase cubic alloy of this system was obtained up to the composition of Ti$_{0.90}$Mo$_{0.10}$C [8], then in [10] it was shown that it is possible to obtain this alloy by the method of powder metallurgy with the following contents of the components Ti$_{0.74}$Mo$_{0.26}$C and Ti$_{0.70}$Mo$_{0.30}$C. These alloys have a NaCl-type crystal structure with lattice parameters $a = 4.330 \pm 0.001$ and $a = 4.338 \pm 0.001$ Å, respectively. Since the chemical compositions of the obtained alloys are new, it is of interest to study their properties. One of the fundamental properties of a solid is the RMSD of its atoms from their equilibrium position due to thermal vibrations [11]. According to [10], the crystal structure of Ti$_{0.70}$Mo$_{0.30}$C is cubic with clearly pronounced strong intensities of diffraction maxima in the neutron diffraction pattern. The same can be said about the neutron diffraction pattern of the Ti$_{0.74}$Mo$_{0.26}$C alloy. Such neutron diffraction patterns with strong diffraction peak intensities make it possible to determine the RMSD of atoms in a given alloy with high reliability and accuracy. The aim of this work is to determine the crystal structure and RMSD of atoms of the Ti$_{0.74}$Mo$_{0.26}$C and Ti$_{0.70}$Mo$_{0.30}$C alloys by neutron diffraction.

2. Experimental
The samples Ti$_{0.74}$Mo$_{0.26}$C and Ti$_{0.70}$Mo$_{0.30}$C were obtained by powder metallurgy by sintering mixed powders of cubic carbides TiC and MoC in appropriate proportions. Cubic carbides of titanium TiC and molybdenum MoC were obtained by self-propagating high-temperature synthesis [12]. Cubic titanium and molybdenum carbide powders were thoroughly mixed for 4 h in an agate mortar. The average particle size of the powders was $r = 40 \, \mu\text{m}$. Next, a cylindrical briquette was prepared from the mixed powders at a pressure of $3 \times 10^6 \, \text{N/m}^2$. The prepared briquette was annealed in a high-temperature vacuum furnace of the SSHV - 1.2.5/25 I1 type at $2200^\circ\text{C}$ in a graphite cup for 8 h, then cooled together with the furnace [10]. The samples are sintered alloys of cylindrical shape with a size of $8 \times 70 \, \text{mm}^2$. The chemical composition of the synthesized samples was determined by chemical analysis, as well as by minimizing the divergence factors of the experimental and calculated diffraction reflection intensities on the neutronogram of the sample. The accuracy of chemical analysis is 0.3%. X-ray diffraction was used to evaluate the homogeneity of the samples according to the crystal structure because of its higher angular resolution [13]. For this purpose, X-ray diffractograms of the samples were taken on an X-ray diffractometer DRON-3M with the use of Cu$K_\alpha$ radiation in the interval of Bragg angles $2\theta = 10^\circ$-$110^\circ$ with the detector rotation speed of 1 deg/min (Ni-filter, $\lambda = 1.5418 \, \text{Å}$). To determine the lattice parameters from the X-ray image, we used imaging of a narrow range of angles near the diffraction maximum with a detector rotation speed of 1/4 deg/min at $2\theta > 101^\circ$. Neutron diffraction was chosen as the main method for determining the RMSD of atoms in the Ti$_{0.70}$Mo$_{0.30}$C alloy, which equally allows us to obtain more reliable information about the position of heavy (metals) and light atoms (nonmetals) in the crystal lattice of powder samples [14, 15].

Neutron diffraction patterns were obtained using the neutron diffractometer mounted at the thermal column of the atomic reactor of the INP AS RUz ($\lambda = 1.085 \, \text{Å}$) [16]. The ratio of the intensities of the strongest diffraction maximum from the Miller index plane (111) and the background of the reference Ni sample with a cubic structure at a full vanadium cassette of $8 \times 70 \, \text{mm}^2$. The neutronogram was measured so that the statistical error in determining the integral intensity of the diffraction maxima was from 3 to 5%, depending on the position of the maxima along the Bragg angle axis. The neutronogram of the sample was taken three times each, in order to exclude random error. In addition, before and after measuring the neutronogram of the sample, the neutronogram of the reference Ni sample was measured to verify the validity of the neutronographic data.

To process the neutronogram, we used the method of full-profile analysis of diffractograms proposed by the International Association of Crystallographers [17]. The RMSD of the atoms in the alloy was determined by both linear and nonlinear least squares methods. The nonlinear least squares method in crystallography is called full-profile analysis of diffractograms (Rietveld method). This method of processing diffractograms is attractive because it includes all refined structural, profile and instrumental parameters in the formula of the profile function non-linearly. The function parameters including structural, instrumental and other characteristics are also refined using the nonlinear least squares method [18].

### 3. Experimental results and discussion

Neutron diffraction pattern of alloy Ti$_{0.74}$Mo$_{0.26}$C in Fig. 1. The alloy Ti$_{0.30}$Mo$_{0.70}$C has similar neutron diffraction pattern. The neutron diffraction patterns of the alloys are well explained in the framework of sp. gr. Fm$\bar{3}$m, where Ti and Mo atoms are interchanged and statistically arranged in positions 4 ($b$), and C atoms are arranged in octahedral positions 4 ($a$). The results of neutron structural analysis are consistent with the data of [10].

For a cylindrical forms polycrystalline sample, the experimentally observed neutron diffraction reflection intensity for a cubic structure, as follows from the structural factor expression given for sp. gr. Fm$\bar{3}$m in [19], is ultimately determined by the following expression:

$$I(hkl) = I_0 \frac{N_0}{N} \frac{S(hkl)}{S_0} \frac{\cos^2 \theta}{h^2 + k^2 + l^2} \frac{1}{d^2}$$
where \( I_0 \) is the calculated intensity of the diffraction maximum without taking into account the thermal factor (RMSD atoms), \( k \)-coefficient that depends on the geometry of the apparatus and the sample; 
\[
\overline{u_z^2} = \frac{u_{Ti}^2 + u_{Mo}^2 + u_{C}^2}{3}
\]
- averaged RMS displacement of an atomic complex (hereafter atom), each consisting of the RMS amplitude of thermal vibrations of the atoms and static distortions of the lattice: 
\[
\overline{u_i^2} = u_{dy}^2 + u_{stat}^2
\]

Figure 1. Neutron diffraction pattern of alloy Ti_{0.74}Mo_{0.26}C: Dots - experiment, solid line - calculation within the framework of space group (sp. gr.) Fm\(\overline{3}m\), \(\Delta\) - difference between calculated and experimental intensities. Above peaks Miller indexes of the reflecting planes are indicated.

The static displacement of atoms from the ideal position arises due to differences in the size of the atoms and deviation of the alloy composition from stoichiometry. According to expression (1), the graph of the dependence of \(\ln(I_{exp}/I_{calc})\) on \(\sin^2 \theta / \lambda^2\) is a straight line, the slope of which can be used to determine the thermal factor \(2B\):

\[
2B = -\frac{16\pi^2 \overline{u_z^2}}{3}
\]

Then we use formula (2) to determine the RMS displacement \(\overline{u_z^2}\). The strongest diffraction maxima were used to construct dependence (1). Such a method for determining the RMSD of atoms in cubic crystals has recently been widely used in neutronography, and has become a widely accepted method [14, 21]. In principle, the RMS displacement of atoms in cubic crystals can also be determined by other methods: X-ray diffraction, colorimetry, through mechanical properties. However, the neutronographic method of RMSD determination has a number of advantages over other methods. First, this method is attractive because \(\overline{u_z^2}\) is determined directly from the experiment without any
intermediate calculations. Second, the neutron scattering amplitude is independent of the Bragg angle, neutron absorption in substances is negligible, the extinction effect can be neglected, and neutron scattering occurs directly on nuclei [22]. All of these factors make it possible to significantly increase the accuracy and reliability of determining the $u^2$ value. The advantages of the neutron diffraction method of RMSD determination were also noted in [23]. The dependence of the straight line

$$\ln\left(\frac{I_{\text{exp}}}{I_o}\right) \times \frac{\sin^2 \theta}{\lambda^2}$$

is shown in Fig. 2. The slope of the straight line $\ln(I_{\text{exp}} / I_{\text{calc}})$ was determined by the method of least squares. Then, using formula (2), we calculated the RMS displacement of atoms in the alloys. It is $u^2 = 0.101 \pm 0.002$ Å for Ti$_{0.76}$Mo$_{0.24}$C and $u^2 = 0.110 \pm 0.003$ Å for the Ti$_{0.70}$Mo$_{0.30}$C composition.

Figure 2. Dependence of $\ln\left(\frac{I_{\text{exp}}}{I_o}\right) \times \frac{\sin^2 \theta}{\lambda^2}$ for the alloy a) Ti$_{0.70}$Mo$_{0.30}$C and b) Ti$_{0.74}$Mo$_{0.26}$C.

The Miller indices of the reflecting planes $hkl$ (sp. gr. Fm$\overline{3}$m) are indicated above the points. The value of the RMS displacement of atoms in alloys Ti$_{0.74}$Mo$_{0.26}$C and Ti$_{0.70}$Mo$_{0.30}$C is significantly greater compared with the RMS displacement of atoms in binary TiC carbide ($u^2 = 0.084 \pm 0.003$) [24]. The increase in the averaged total RMSD of atoms in alloys of the Ti-Mo-C system cannot be explained by an increase in the amplitude of thermal vibrations $u_{\text{dyn.}}^2$, since it is inversely proportional to the mass of the element, and in this case a significant portion of the relatively light-mass Ti atoms have been replaced with heavy Mo atoms. The observed pattern can be explained with the occurrence of static distortions in the lattice of alloys Ti$_{0.74}$Mo$_{0.26}$C and Ti$_{0.70}$Mo$_{0.30}$C due to the replacement of a significant portion of the relatively light atom Ti with heavy atom of Mo in alloy TiC.

We also determined the micro-hardness of the alloy Ti$_{0.70}$Mo$_{0.30}$C. The sample of cylindrical shape was 15×10 mm$^2$ in size. The size of the prints was measured 20 times and each time the micro-hardness was determined, then the average value was obtained. After correcting for porosity, the micro-hardness of the Ti$_{0.70}$Mo$_{0.30}$C alloy was $H_v = 38 \pm 1.4$ GPa. For comparison, we note that according to [25], the micro-hardness of pure titanium carbide TiC is $H_v=32 \pm 1.7$ GPa. Apparently, the resulting larger static distortions in the Ti$_{0.70}$Mo$_{0.30}$C alloy compared to TiC leads to a significant increase in micro-hardness.
4. Conclusions.
The possibility of obtaining alloys Ti\text{0.74}Mo\text{0.24}C, Ti\text{0.70}Mo\text{0.30}C by powder metallurgy has been shown. The crystal structure of this alloy is described within the framework of sp. gr. Fm\bar{3}m, in which titanium and molybdenum atoms are interchanged and statistically occupy positions 4\text{b}, and carbon atoms statistically occupy octahedral positions 4\text{a}. Replacement of a large part of titanium atoms with molybdenum in titanium carbide TiC does not lead to a change in its crystal structure.

The averaged total RMS displacement of atoms in Ti\text{0.74}Mo\text{0.26}C and Ti\text{0.70}Mo\text{0.30}C alloys was determined from neutron diffraction data by least-squares and full-profile analysis methods. It is shown that the replacement of part of the Ti atoms in the cubic titanium carbide TiC leads to the appearance of static distortions in the lattice of the cubic three-component alloy Ti\text{0.70}Mo\text{0.30}C. This leads to an increase in the total RMS displacement of the alloy atoms compared to the cubic binary TiC alloy.

It is established that after correcting for porosity the microhardness of Ti\text{0.70}Mo\text{0.30}C alloy is \(H_v = 38 \pm 1.4\) GPa, which is 19% higher than the microhardness of pure TiC carbide. Apparently, the resulting larger static distortions in the Ti\text{0.70}Mo\text{0.30}C alloy compared to TiC result in higher microhardness. Consequently, replacing part of the Ti atoms with Mo in the lattice of titanium carbide TiC may be a way to change the dynamic characteristics of its crystal lattice.

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