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Article

Effect of Carbon and Nitrogen Concentration on the Superconducting Properties of $(\text{NbMoTaW})_1\text{C}_x\text{N}_y$ Carbonitride Films

Gabriel Pristáš ¹, Slavomír Gabáni ¹, Petra Hviščová ², Jozef Dobrovodský ³, Dmitry Albov ², Maksym Lisnichuk ², Oleksandr Onufrienko ¹, Janina Zorych ^{1,4}, František Lofaj ² and Karol Flachbart ^{1,*}

¹ Institute of Experimental Physics of the Slovak Academy of Sciences, Watsonova 47, 04001 Košice, Slovakia

² Institute of Materials Research of the Slovak Academy of Sciences, Watsonova 47, 04001 Košice, Slovakia

³ Advanced Technologies Research Institute, Slovak University of Technology in Bratislava, Trnava, Slovakia

⁴ Faculty of Electrical Engineering and Informatics, Technical University, SK-04200 Košice, Slovakia

* Correspondence: flachb@saske.sk

Abstract

We report about the effect of nitrogen and carbon concentration on the superconducting transition temperature T_c of $(\text{NbMoTaW})_1\text{C}_x\text{N}_y$ carbonitride films deposited using reactive DC magnetron sputtering. By measuring the temperature dependence of electrical resistance and magnetization of these carbonitrides, with $0.20 \leq x \leq 1.17$ and $0 \leq y \leq 0.73$, we observe a T_c enhancement that occurs especially at high ($x \geq 0.76$) carbon concentrations, with the largest $T_c = 9.6$ K observed in the over-doped fcc crystal structure with $x = 1.17$ and $y = 0.41$. The reason why the largest T_c appears at high carbon concentrations is probably related to the lower atomic mass of carbon compared to nitrogen and to the increase of the electron-phonon interaction due to different bonding of carbon (compared to nitrogen) to the Nb-Mo-Ta-W metallic sublattice. However, as for concentrations $y > 0.71$ and $x + y > 1.58$ two structural phases begin to form, also the proximity to structural instability may play a role in the observed T_c enhancement. Additional measurements in magnetic field show that the upper critical fields B_{c2} of $(\text{NbMoTaW})_1\text{C}_x\text{N}_y$ carbonitrides provide $B_{c2}/T_c < 2$ T/K ratios, which are within the weak-coupling pair breaking limit.

Keywords: high and medium entropy carbonitrides; superconductivity; superconducting transition temperature; upper critical field

1. Introduction

Superconductivity in compounds consisting of transition metal (TM) elements and nonmetals as carbon and nitrogen has been known since 1930 [1]. Later on, extensive research related to superconductivity in carbides and nitrides has been performed, and it was shown that superconductivity can be observed in several transition metals carbides or nitrides (see e.g. [2-6]), in transition metal alloy carbides or nitrides (see e.g. [7,8]), and in carbonitrides containing both carbon and nitrogen (see e.g. [9]). Among TM carbides and nitrides the highest transition temperatures have been observed in molybdenum carbide MoC with a superconducting transition temperature T_c of ~ 14.3 K [4] and niobium nitride NbN with a T_c of ~ 17.3 K [3], which are much higher as that for pure Mo and Nb with 0.92 K and 9.2 K, respectively. For niobium carbonitrides the highest $T_c \approx 16.9$ K was observed for the $\text{NbC}_{0.3}\text{N}_{0.7}$ composition [9]. It is necessary to add that all the mentioned above TM carbides and nitrides can be considered as conventional weak-coupling s-wave phonon mediated Bardeen-Cooper-Schrieffer (BCS) superconductors, in which in the simplest case the T_c dependence may be described using the relation $k_B T_c = 1.13 \hbar \omega_D \exp(-1/N(E_F)V)$ (see e.g. [10]), where ω_D denotes the phonon Debye frequency, $N(E_F)$ the electronic density of states (DOS) at the Fermi energy E_F , V

the electron-phonon interaction potential, and k_B and $\hbar$ the Boltzmann and Planck constant, respectively.

Very recently, multicomponent materials as high entropy alloys (HEAs), containing five or more metallic elements in near-equiatomic proportions, and high entropy ceramics (HECs), which in addition to metallic ones also contain non-metallic atoms as e.g. carbon and nitrogen, have begun to be investigated [11-14]. The reason for this is that in HEAs and HECs, due to the cocktail effect coming from synergy phenomenon of constituent atoms (having a different number of valence electrons, different atomic radii and a high mixing / configurational entropy that represents a measure of the number of ways in which a particular configuration of metal atoms can be achieved), also new and unexpected results can be expected. Overviews of unique properties of HEAs and HECs can be found e.g. in [15-17], reviews and new knowledge about their superconducting properties e.g. in [18-21]. It has to be added that investigated were also RE123 high- T_C superconductors with a HEA-type of the rare earth (RE) site ($Y_{0.28}Nd_{0.16}Sm_{0.18}Eu_{0.18}Gd_{0.20}Ba_2Cu_3O_{7-\delta}$ and $Y_{0.18}La_{0.24}Nd_{0.14}Sm_{0.14}Eu_{0.15}Gd_{0.15}Ba_2Cu_3O_{7-\delta}$, see [22]) which exhibit transition temperatures exceeding 90 K.

Regarding high entropy carbides, e.g. in [12] superconductivity at 2.35 K and topological properties in $(Ti_{0.2}Zr_{0.2}Nb_{0.2}Hf_{0.2}Ta_{0.2})C$ HEC is reported. Related density functional theory (DFT) calculations show that six type-II Dirac points exist in this material, and due to the stability of the structure, robust superconductivity under pressure in this HEC superconductor is also observed. Similarly, in [13] the authors designed and produced a sequence of original bulk $(Ti_{0.2}Nb_{0.2}Ta_{0.2}Mo_{0.2}W_{0.2})C_{1-x}N_x$ ($0 \leq x \leq 0.45$) superconductors, and observed that these high entropy carbonitrides possess type-II Dirac points in the electronic band structure which imply that they have a potential as candidates to bridge superconductivity with topology. These discoveries indicate that the physical properties and potential applications establish HE carbonitrides as a promising platform for exploring unconventional physics. On the other hand, in [14] it was shown that with the rise of nitrogen concentration x in $(TiNbMoTaW)_{1.0}N_x$ nitride films a large increase of T_C is observed, from 0.62 K for $x = 0$ up to 5.02 K for $x = 0.74$. The observed high T_C enhancement and the dome-like T_C vs x dependence have been attributed to the phonon frequency increase due to incorporation of light N atoms and to the simultaneous strengthening of the electron-phonon interaction that probably develops due to the high configuration entropy in this HEM. This high configuration entropy namely offers lots of options for N atoms to find the thermodynamically most appropriate positions in the lattice, and thus to create a suitable phonon mode distribution and thus strengthen the electron-phonon interaction.

As introduction of carbon and nitrogen greatly affects the properties of medium and high entropy materials, the aim of the current work is to investigate the impact of C and N incorporation on the superconducting properties of NbMoTaW, mainly their impact on the transition temperature T_C . The choice of this medium entropy alloy was based on the fact that practically all possible constituents of this MEA are superconducting, the TM elements (Nb: $T_C \approx 9.2$ K, Mo: $T_C \approx 0.92$ K, Ta: $T_C \approx 4.4$ K, W: $T_C \approx 0.01$ K), the corresponding carbides (NbC: $T_C \approx 11$ K, MoC: $T_C \approx 14.3$ K, TaC: $T_C \approx 10$ K, WC: $T_C \approx 10$ K), as well as the corresponding nitrides (NbN: $T_C \approx 17.3$ K, MoN: $T_C \approx 5.8$ K, TaN: $T_C \approx 6$ K). In tungsten nitride a T_C of about 4.85 K was observed in nitride films close to the phase boundary between β -W and W_2N [23]. On the other hand, based on first-principles calculations [24] it was shown that superconductivity in WN can be found and its T_C enhanced significantly to about 31 K through electron doping.

In this contribution, we analyze and discuss in detail the investigations of the superconducting properties of sputtered $(NbMoTaW)_{1.0}C_xN_y$ films within a wide range of carbon (x) and nitrogen concentration (y) values. The obtained results show a threefold T_C enhancement through C and N incorporation, nevertheless, it appears that carbon concentration plays the dominant role in this enhancement. This is probably related to the lower atomic mass of C compared to N and to the parallel increase of the electron-phonon interaction due to the different bonding of carbon atoms (compared to nitrogen) to the metallic NbMoTaW sub-lattice. However, as the highest T_C values are

observed at the boundary between one-phase and two-phase crystal structures, it may indicate that the T_c enhancement is additionally related to the proximity of structural instability. It should be added that some results on these carbonitride films have been published [25], this mainly concerns their composition, structure and mechanical properties.

2. Materials and Methods

Two series of films with different C and N concentrations were deposited in the Cryofox 500 system (Polyteknik, Denmark) using a NbMoTaW target with composition 25:25:25:25 at% (99.9% purity) and a C target (99.9% purity) having a diameter of 76.2 mm and 4 mm thickness (Testbourne Ltd., UK). However, additional ToF ERDA measurements on the target revealed its contamination by ~15 at% of carbon, most probably from the previous depositions involving carbon and/or hydrocarbons. The substrates were polished (0001) sapphire wafers (diameter - 50.8 mm, thickness - 430 μm) heated to a temperature of 500 °C without any bias voltage. The film deposition parameters were optimized for metallic films and included 300 W of DC power on the NbMoTaW target and a constant deposition time of 15 min. In series I, the only variable was the flow of nitrogen, x , added to the Ar sputtering atmosphere. It varied from 0 sccm up to 5 sccm with a 1 sccm step. In series II, a power of 600 W was used to sputter carbon from the C - target.

The structure of the sputtered films was investigated using scanning electron microscopy (SEM) devices FESEM/FIB Auriga Compact and EVO MA 15, Zeiss, Germany. In parallel, X-ray measurements were made on a Rigaku Ultima IV with parallel beam $\text{CoK}\alpha$ radiation in a symmetrical θ - θ (Bragg-Brentano, B-B) and additional grazing incidence (GI) with fixed incident beam angle of 5° scan modes to eliminate diffraction from single-crystal sapphire substrate. Crystalline phases were identified using the Crystal-Impact Match! software, unit cell parameters were refined in a Full-Profit program package. $\text{CoK}\alpha$ measurements were recalculated to correspond to $\text{CuK}\alpha$ radiation. The texture was analyzed by comparing experimental diffractograms from B-B scans with GI scans and theoretically calculated texture-free diffractograms.

The chemical composition of the films was determined using Time-of-Flight Elastic Recoil Detection Analysis (ToF-ERDA) at the telescope of the 6 MV tandem ion accelerator and $^{197}\text{Au}^{8+}$ analyzing beam with an energy of 45 MeV [26]. Recoiled ions from the sample were detected by the TOF-ERDA spectrometer with a Gas Ionizing Chamber with an analysis sensitivity of 0.02 at. %. More details about the films preparation and their characterization can be found in Ref. [25].

The electrical resistance of the films has been measured using a probe alternating current method in a ^4He cryostat with variable temperature insert in the temperature range from 300 K down to about 1.8 K. The electrical contacts were made using four spring contacts. During the measurements in magnetic field with different intensities, the field was oriented perpendicularly to the film/substrate plane. Magnetization measurements between 2 K and 300 K in a field B of 1 mT were carried out in a commercial magnetic property measurement system (MPMS, Quantum Design).

3. Additional comments to the choice of the target composition

An important parameter that has to be considered when designing a suitable initial HEA for subsequent HEA carbonization or/and nitridation is the ability of HEA - metals to form thermodynamically stable carbon or nitride compounds, which varies along the periodic table (see e.g. [27,28]). This ability points to strong carbide formers for all metals (Nb, Mo, Ta and W) of our initial HEA, and to strong nitride formers found in group 5 of the periodic table, as e.g. Nb and Ta. On the other hand, metals in group 6, as e.g. Mo and W are considered as weak nitride formers. Highly stable transition metal nitrides, based on strong nitride formers, are typically so-called interstitial compounds where N atoms at low concentration can occupy voids in the metal structure. At higher N concentrations these interstitial compounds usually transform into a NaCl-type (*fcc*) crystal structure. Whereas on contrary the nitride bond strength decreases to the right of the periodic

table, the formation enthalpy of *fcc*-type nitrides also decreases and more complex structures with other stoichiometries become more common. The reason for this trend is the filling of anti- and non-bonding electronic states as the valence electron count increases [29]. Examples of complex nitride structures can be found e.g. also among tungsten nitrides which include hexagonal WN, W₂N, W₅N₄, W₅N₈, rhombohedral W₂N₃, W₇N₆ or cubic W₃N₄ structures [30]. Nevertheless, due to the limited atom mobility during film deposition methods, such complex structure formation is not expected.

Another important parameter which has to be considered is related to the atomic size differences of HEA constituents, namely, HEAs with increasing atomic size difference prefer to form the *bcc* structure instead of the *fcc* one (see e.g. [31,32]). This preference comes from the ability of the *bcc* structure to accommodate larger atomic size differences with lower strain energy. If the average deviation from the composition-weighted average atomic radius of the included metals $\delta = (\sum c_i (1 - r_i/r_a)^2)^{1/2}$, where $r_a = \sum c_i r_i$ is the composition-weighted average atomic radius, and c_i and r_i the atomic percentage and atomic radius of the *i*-th element, exceeds a threshold value of $\delta \approx 6.4\%$, the *bcc* $\rightarrow$ *fcc* transition during nitridation or carbonization of HEAs may not happen [28,31,32]. When calculating this deviation for the case of Nb₂₅Mo₂₅Ta₂₅W₂₅ with atomic radius data taken from [33] (with Nb: $r_i = 143$ pm, Mo: $r_i = 136$ pm, Ta: $r_i = 143$ pm, W: $r_i = 137$ pm) a deviation of $\delta \approx 4.7\%$ can be obtained, which lies below the 6.4 % threshold. Thus, from this point of view there should be no obstacles to the formation of the *fcc* phase in corresponding carbides or nitrides.

4. Results and discussion

4.1. Composition and structure

The crystal structure of investigated (NbMoTaW)₁C_xN_y films, which are described in more details in [25], as well as their composition are given in Table 1. It can be seen that the transition from the *bcc* structure of the initial (NbMoTaW)₁C_{0.2}N₀ HEA metal (polluted by carbon) to the NaCl-like *fcc* structure of (NbMoTaW)₁C_xN_y films is observed in the concentration range $0 < x + y < \sim 0.5$. At higher $x + y$ concentrations the films exhibit a *fcc* crystal structure, however, for high C concentration ($x > 1.17$) this structure contains also C-clusters, and for high N concentration ($y > 0.71$) an additional hexagonal close-packed structure (*hcp*) begins to emerge. A schematic visualization of the expected *fcc* structure of (NbMoTaW)₁C_xN_y carbonitrides is shown in Fig. 1. Illustrated is the case with $(x + y)/M < 1$, i.e. when the ratio between the concentration of carbon and nitrogen atoms ($x + y$) and the concentration of metal atoms ($M = \text{Nb} + \text{Mo} + \text{Ta} + \text{W} = 1$) is sub-stoichiometric and also contains vacancies.

Table 1. Overview of data obtained from performed investigations on (NbMoTaW)₁C_xN_y films. The first column indicates the sample composition determined by ToF ERDA, the name of the corresponding sample from [25] and the measurements performed on this sample. The second column shows the dominating crystal structure of the film (here *bcc* stands for body-centered cubic, *fcc* for face-centered cubic, and *hcp* for hexagonal close-packed). In the next columns, R_{300}/R_0 shows the resistance ratio, where R_{300} denotes the film resistance at 300 K and R_0 the resistance just above the T_c onset, T_c denotes the superconducting transition temperature (in parentheses the transition onset value for two samples is given), and B_{c2} the upper critical field in Tesla. The last column represents the valence electron count (VEC), i.e. the average number of valence electrons per atom in el./atom (including metal, carbon and nitrogen atoms). Sign n.d. in some cells means *not determined*.

sample composition (sample label in [25]), measurements	crystal structure	R_{300}/R_0 (RRR)	T_c [K]	$B_{c2}(0)$ [T]	VEC el./at.
Series I					
(Nb _{0.23} Mo _{0.24} Ta _{0.26} W _{0.27}) _{1.0} C _{0.20} N _{0.0} (4ME-C(0)-0N-a), $R(T)$, $M(T)$	<i>bcc</i>	1.004	3.25	4.05	5.235
(Nb _{0.24} Mo _{0.25} Ta _{0.25} W _{0.26}) _{1.0} C _{0.24} N _{0.23}	<i>bcc</i> with	0.989	2.49	2.70	5.180

(4ME-C(0)-1N), R(T)	<i>fcc</i>				
(Nb _{0.24} Mo _{0.25} Ta _{0.25} W _{0.26}) _{1.0} C _{0.25} N _{0.43}	<i>fcc</i>	0.975	3.90	3.94	5.141
(4ME-C(0)-2N), R(T)					
(Nb _{0.24} Mo _{0.26} Ta _{0.25} W _{0.25}) _{1.0} C _{0.24} N _{0.55}	<i>fcc</i>	0.940	4.83	6.55	5.140
(4ME-C(0)-3N), R(T)					
(Nb _{0.24} Mo _{0.26} Ta _{0.24} W _{0.26}) _{1.0} C _{0.24} N _{0.66}	<i>fcc</i>	0.905	5.30	7.57	5.140
(4ME-C(0)-4N), R(T)					
(Nb _{0.24} Mo _{0.26} Ta _{0.24} W _{0.26}) _{1.0} C _{0.26} N _{0.71}	<i>fcc</i>	0.847	5.61	9.16	5.126
(4ME-C(0)-5N), R(T), M(T)					
Series Ib					
(Nb _{0.20} Mo _{0.29} Ta _{0.25} W _{0.26}) ₁ C _{0.29} N _{0.53}	<i>fcc</i>	n.d.	5.2	n.d.	5.108
(new, with N-flow 3N), M(T)					
(Nb _{0.20} Mo _{0.29} Ta _{0.25} W _{0.26}) ₁ C _{0.30} N _{0.58}	<i>fcc</i>	n.d.	5.9	n.d.	5.092
(new, with N-flow 4N), M(T)					
(Nb _{0.20} Mo _{0.29} Ta _{0.25} W _{0.26}) ₁ C _{0.32} N _{0.68}	<i>fcc</i>	0.832	6.3	9.30	5.091
(new, with N-flow 5N), M(T), R(T)					
(Nb _{0.22} Mo _{0.28} Ta _{0.24} W _{0.26}) ₁ C _{0.36} N _{0.73}	<i>fcc</i> with	n.d.	-	-	5.046
(new, with N-flow 7N), M(T)	<i>hcp</i>				
Series II					
(Nb _{0.31} Mo _{0.18} Ta _{0.25} W _{0.26}) _{1.0} C _{0.76} N _{0.0}	<i>fcc</i>	1.001	8.78	9.34	4.816
(4ME-C(500)-0N-a), R(T), M(T)					
(Nb _{0.31} Mo _{0.18} Ta _{0.25} W _{0.26}) _{1.0} C _{0.77} N _{0.0}	<i>fcc</i>	0.939	8.71	8.70	4.807
(4ME-C(600)-0N-b), R(T)					
(Nb _{0.35} Mo _{0.17} Ta _{0.23} W _{0.25}) _{1.0} C _{0.80} N _{0.0}	<i>fcc</i>	0.989	8.28	n.d.	4.931
(4ME-C(700)-0N-c), R(T)			(~9.2)		
(Nb _{0.32} Mo _{0.18} Ta _{0.24} W _{0.26}) _{1.0} C _{1.17} N _{0.41}	<i>fcc</i>	0.939	9.60	13.83	4.707
(4ME-C(600)-2N), R(T), M(T)			(~10.1)		
(Nb _{0.32} Mo _{0.19} Ta _{0.24} W _{0.25}) _{1.0} C _{1.18} N _{1.13}	<i>fcc</i> with	0.599	-	-	4.771
(4ME-C(600)-5N), R(T)	C-clusters				

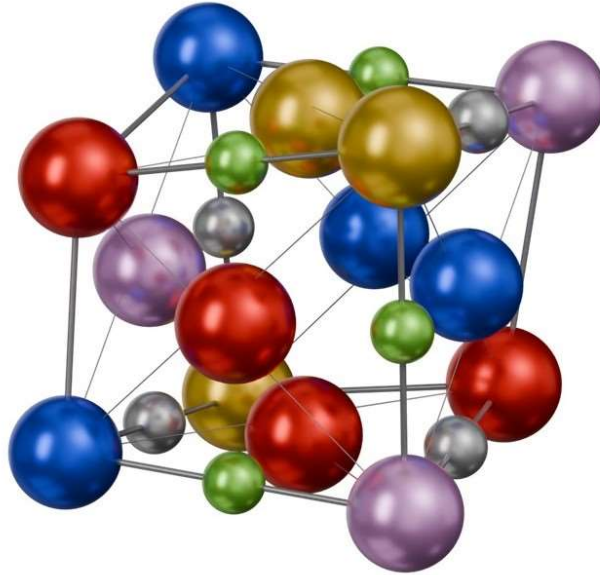


Figure 1. Schematic illustration of the *fcc* structure of $(\text{NbMoTaW})_1\text{C}_x\text{N}_y$ carbonitrides. Illustrated is the case with $(x + y)/M < 1$, i.e. when the ratio between the concentration of carbon and nitrogen atoms $(x + y)$ and the concentration of metal atoms ($M = \text{Nb} + \text{Mo} + \text{Ta} + \text{W} = 1$) is sub-stoichiometric and contains vacancies (unoccupied edges of the cube). Metal atoms are shown by large spheres, carbon atoms by grey and nitrogen atoms by green small spheres.

4.2. Resistance and magnetization results

Fig. 2 shows the temperature dependencies of electrical resistance $R(T)$ of the studied films normalized to their resistance values R_0 just above the superconducting transition temperature onset. Sudden drops of $R(T)/R_0$ to zero represent the transitions into the superconducting state. The relevant T_c value was defined as the temperature at which $R(T)$ reaches 50 % of the normal state resistance R_0 . These resistance superconducting transitions were confirmed for some films by a sharp diamagnetic drop at T_c in parallelly performed magnetization measurements (see Fig. 3). Nevertheless, in $(\text{Nb}_{0.35}\text{Mo}_{0.17}\text{Ta}_{0.23}\text{W}_{0.25})\text{C}_{0.80}\text{N}_0$ and $(\text{Nb}_{0.32}\text{Mo}_{0.18}\text{Ta}_{0.24}\text{W}_{0.26})\text{C}_{1.17}\text{N}_{0.41}$ films of series II with a high carbon concentration, two T_c onsets in the $R(T)/R_0$ dependencies were observed, the higher ones at 9.2 K and 10.1 K, and the lower ones at 8.28 K and 9.6 K, respectively. However, the magnetization measurements (Fig. 3) point to the fact that at T_c values of 8.28 K and 9.6 K, respectively, the entire samples enter a superconducting state. It is necessary to add that the inaccuracy (error) of T_c determination is usually given by the ratio $\Delta(T_c)/T_c$, where $\Delta(T_c)$ represents the range between temperatures at which is $R(T)/R_0 = 0.9$ and $R(T)/R_0 = 0.1$. In our case, for the carbon-rich $(\text{Nb}_{0.35}\text{Mo}_{0.17}\text{Ta}_{0.23}\text{W}_{0.25})\text{C}_{0.80}\text{N}_0$ and $(\text{Nb}_{0.32}\text{Mo}_{0.18}\text{Ta}_{0.24}\text{W}_{0.26})\text{C}_{1.17}\text{N}_{0.41}$ films is $\Delta(T_c)/T_c \approx 3\%$, for other films (showing one sharp phase transitions) is $\Delta(T_c)/T_c \approx 0.5\%$.

All obtained T_c values are shown in Fig. 4, as a dependence of N concentration y (a) and C concentration x . These dependencies indicate that high concentration of carbon plays the dominant role in the about threefold T_c increase. Moreover, one can see that the highest T_c values of 6.3 K for the nitrogen-rich series (with $y \approx 0.7$, see Series Ib) and of 9.6 K for the carbon-rich series (with $x = 1.17$ and $y = 0.41$, see Series II), are observed in samples at the verge of *fcc* structure instability. Namely, at higher concentrations two-phase structures begin to form: a *fcc* + *hcp* structure for $y > 0.71$ (see Series 1b) and a *fcc* + *C-clusters* structure for $x + y > 1.58$ (see Series II). This indicates that in investigated carbonitrides is the T_c enhancement also related to the proximity of structural instability, as predicted in [34].

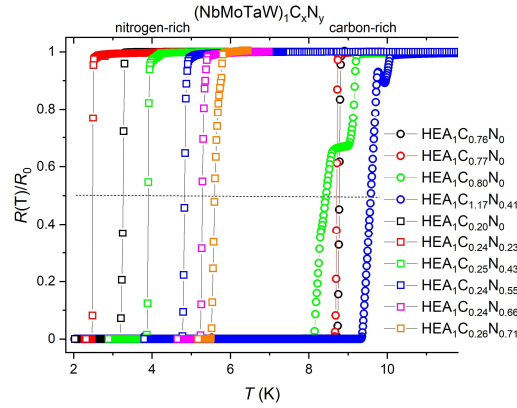


Figure 2. Temperature dependencies of normalized resistance $R(T)/R_0$ for $(\text{NbMoTaW})_1\text{C}_x\text{N}_y$ films in zero magnetic field, where $R(T)$ is the temperature dependence and R_0 the resistance just above the transition temperature onset, respectively. The samples are labelled based on Table 1.

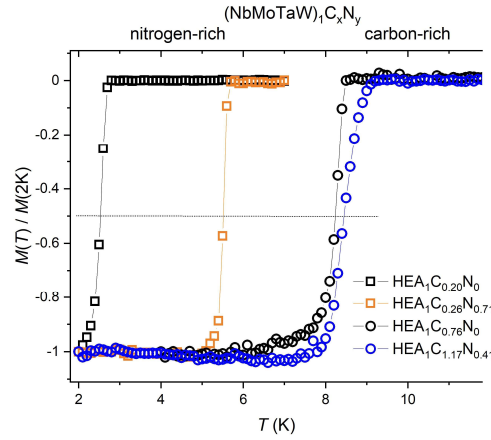
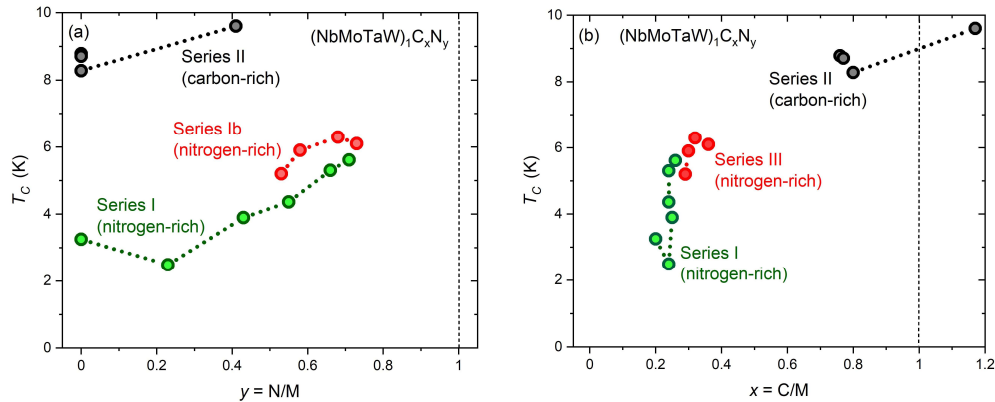


Figure 3. Normalized DC magnetization dependencies $M(T)/M(2K)$ in field of 1 mT for some $(\text{NbMoTaW})_1\text{C}_x\text{N}_y$ films. Samples are labelled based on Table 1.

On the other hand, in the case of samples with a considerably over-stoichiometric sum of N and C concentrations (when $x + y > 2$) no superconducting transition was observed. Reasons for this are discussed in the next part.



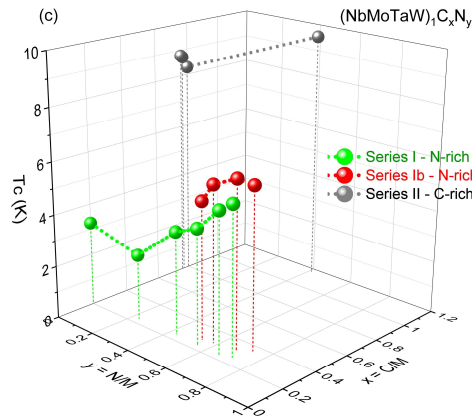


Figure 4. Transition temperature (T_c) dependencies of the $(\text{NbMoTaW})_1\text{C}_x\text{N}_y$ films: (a) - on nitrogen concentration y , (b) - on carbon concentration x , and (c) - as a three-dimensional display of T_c vs $x = \text{C/M}$ and $y = \text{N/M}$.

As can be additionally seen from Fig. 4(a), the T_c dependence on N concentration y in the nitrogen-rich series (Series I) is not monotonic. With increasing y , T_c first decreased from an initial value of 3.25 K to 2.49 K at $y = 0.23$, then gradually increased to a maximum value of $T_c = 5.61$ K at $y = 0.71$. The initial decline of T_c is apparently associated with the transition of the *bcc* structure of the initial HEA lattice to the *fcc* structure of HEA nitrides. The N concentration range in which the *bcc* $\rightarrow$ *fcc* structural change takes place is apparently a region with a high degree of disorder (containing e.g. also a mixture of *bcc* and *fcc* clusters). This high degree of disorder can lead to suppression of superconductivity (see e.g. [35,36]). Furthermore, it was shown in [36] that nonmagnetic impurities destroy superconductivity when the residual resistivity exceeds about $1 \mu\Omega\text{cm}$, i.e. when the carrier mean free path l falls below the superconducting coherence length ξ . To make an estimate, according to [37] can be the Ginzburg-Landau coherence length $\xi_{\text{GL}}(0)$ calculated as $\xi_{\text{GL}}(0) = (\Phi_0/2\pi B_{c2}(0))^{1/2}$, where Φ_0 denotes the magnetic flux quantum and B_{c2} the upper critical magnetic field, which reaches e.g. in $(\text{NbTa})_{0.67}(\text{MoHfW})_{0.33}$ HEA superconductor a value of ~ 15 nm. Simultaneously, the theoretical analysis of the electronic structure of another HEA superconductor $(\text{ScZrNb})_{1-x}(\text{RhPd})_x$, with $0.35 < x < 0.45$ [38], leads to an electron mean free path between 3.2 and 9.2 Å, i.e. to an $l < 1$ nm. Thus, the high degree of disorder that is apparently present in the *bcc* $\rightarrow$ *fcc* structural transition area is likely the main cause for the observed T_c suppression.

The second series of nitrogen-rich films (Series Ib), in which a higher nitrogen concentration was achieved, exhibits the highest T_c value of 6.3 K in the *fcc* phase with $x = 0.68$ (see Fig. 4). But, at higher N concentration ($x = 0.73$) a two-phase (*fcc* + *hcp*) crystal structure forms and T_c starts to decrease. This points to the fact that the highest T_c is observed in the *fcc* phase, but near the border between the *fcc* and (*fcc* + *hcp*) phases.

Results on carbon-rich coatings, on the other hand, show that carbon incorporation leads to a substantially higher T_c increase than in the case of nitrogen. According to the conventional Bardeen-Cooper-Schrieffer (BCS) theory of superconductivity, the stronger influence of carbon than nitrogen can be attributed to its lower atomic mass which may lead to an increase in the phonon frequency. However, also the enhancement of the electron-phonon interaction due to a different valence electron count (VEC) of carbon (having a $\text{VEC}(\text{C}) = 4$, see the periodic table of elements) and nitrogen (in this case $\text{VEC}(\text{N}) = 5$) and thus a different bonding between carbon-to-metal (compared to nitrogen-to-metal) atoms may play an important role. Thus, even if the carbon and nitrogen influence the transition temperature similarly, the more pronounced T_c enhancement by carbon seems to be a result of a combination of its lower mass, the different configuration of its valence electrons, and subsequently a stronger electron-phonon interaction. And also in this case, the highest $T_c = 9.6$ K is

obtained in the *fcc* phase and at the border between two phases, between the *fcc* phase and the (*fcc* + *C-clusters*) phase for $x + y > 1.58$ (see Table 1, Series II).

Moreover, with increasing nitrogen and carbon concentrations, there is a tendency to a semiconducting-like temperature dependence of resistance (i.e. with $R_0 > R_{300}$, see the R_{300}/R_0 ratios in Table 1), caused by the localization of conduction electrons through their bonding to incorporated N and C atoms.

4.3. T_c vs VEC - transition temperature dependence on the valence electron count

To take a closer look how T_c develops with the overall VEC of studied high entropy alloy carbonitrides (i.e. including N atoms with VEC = 5 and C atoms with VEC = 4), Fig. 5 shows this dependence for the above-discussed $(\text{NbMoTaW})_1\text{C}_x\text{N}_y$ films. The upper grey trend line in this figure with a dome-like shape represents the T_c vs VEC dependence for transition metals and their alloys in the crystalline form taken from ref. [39]. This trend line is often referred to as the Matthias T_c vs VEC rule and exhibits a maximum of $T_{Cmax} \approx 11$ K near VEC ≈ 4.7 el./atom (a second dome-like dependence, not shown here, with a maximum of $T_{Cmax} \approx 16$ K is formed at VEC ≈ 6.5 el./atom, see e.g. also [18, 20]).

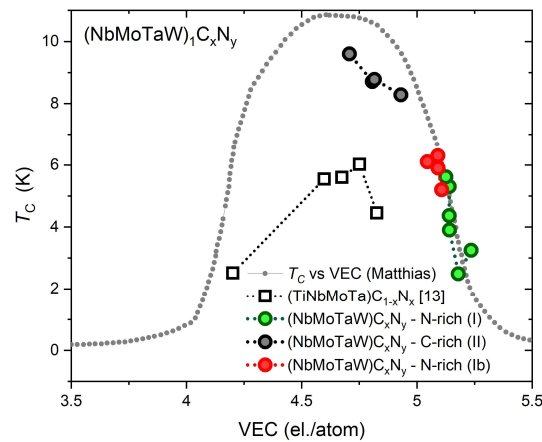


Figure 5. T_c vs VEC dependencies for investigated carbonitrides. The upper grey line with a dome-like shape shows the T_c vs VEC dependence (Matthias rule) for transition metals and their alloys in the crystalline form taken from [39]. Grey points represent Series II, green and red points the Series I and Series Ib of $(\text{NbMoTaW})_1\text{C}_x\text{N}_y$ films. Black squares show the approximative course for the bulk $(\text{Ti}_{0.2}\text{Nb}_{0.2}\text{Ta}_{0.2}\text{Mo}_{0.2}\text{W}_{0.2})\text{C}_{1-x}\text{N}_x$ ($0 \leq x \leq 0.45$) superconductors [13]. The point-connecting dotted lines are the guide to the eyes.

From the displayed T_c vs VEC dependencies one can see that all carbonitrides lie inside the dome bordered by the trendline [39] (including the carbonitrides studied in [13]). Thus, also from here it turns out that incorporations of N and C into HEAs have a different impact, and that high C concentration leads to a more pronounced T_c enhancement. However, as e.g. the T_c of MoC (with a total VEC = 5) reaches a value of 14.3 K, which exceeds the value of $T_{Cmax} \approx 11$ K, it is not excluded that also some HEA alloy carbonitrides or carbides will not obey the Matthias T_c vs. VEC rule [39] and provide a higher T_c .

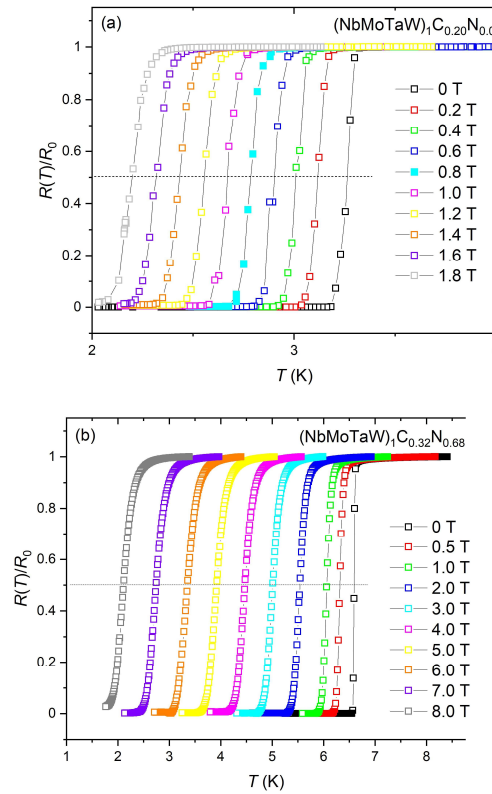
It should be also noted that in $(\text{HEA})_1\text{C}_x\text{N}_y$ films with a significantly over-stoichiometric sum of (N + C) concentrations (i.e. with $x + y > 2$, not shown in Table 1) no superconducting transition was observed. This is probably related to the strong localization of otherwise mobile (conduction) electrons of the metallic sublattice due to their bonding to the high (considerably over-stoichiometric) concentration of C and N atoms. This localization leads namely to an insulating state, which was for the case of these two samples documented by the observation of a sharp increase of their electrical resistance with decreasing temperature. Very similar results, related to the localization of conduction electrons, were recently observed in zirconium nitrides ZrN_y with various N concentrations [40],

where a strongly insulating state was detected at the over-stoichiometric concentrations of nitrogen ($y > 1.15$).

4.4. Upper critical magnetic field B_{c2}

To obtain more information about the superconducting properties of the $(\text{NbMoTaW})_1\text{C}_x\text{N}_y$ films, resistance $R(T)$ measurements in different magnetic fields B were carried out. Fig. 6a shows the $R(T)$ dependence of these films exposed to magnetic fields between 0 T and 8 T, demonstrating the decrease of T_c with increasing B . As a criterion for the T_c determination in magnetic fields, we used again the temperature value at which 50 % of the normal state resistance R_0 just above T_c is reached. From these results we constructed the corresponding upper critical magnetic field B_{c2} vs T phase diagrams (see Fig. 6d). The observed B_{c2} vs T dependencies were described by the Werthamer-Helfand-Hohenberg (WHH) model [41], which e.g. for a nitrogen-rich sample with $x = 0.26$ and $y = 0.71$ ($T_c = 5.61$ K) provides a B_{c2} value of 9.16 T and for a carbon-rich sample with $x = 1.17$ and $y = 0.41$ ($T_c = 9.6$ K) a B_{c2} value of ~ 13.8 T. On the other hand, the nitrogen-free HEA ($x = 0$) shows a B_{c2} value of ~ 4 T.

Thus, the determined zero-temperature $B_{c2}(0)$ values (see Table 1) provide $B_{c2}(0)/T_c$ ratios below 1.86 T/K and point to the fact that the upper critical field in the investigated HEA nitrides does not exceed the weak-coupling Pauli paramagnetic pair breaking limit. Namely, in the weak-coupling BCS theory of superconductivity, the Pauli paramagnetic pair breaking limit is $B_{\text{Pauli}} = \Delta(0)/(\sqrt{2}\mu_B) \approx 1.86[T/K] \cdot T_c$, with μ_B being the Bohr magneton and $\Delta(0)$ the superconducting gap at $T = 0$ (see e.g. [42,43]). The mentioned Pauli paramagnetic limit may be different for strong-coupled superconductors [44,45].



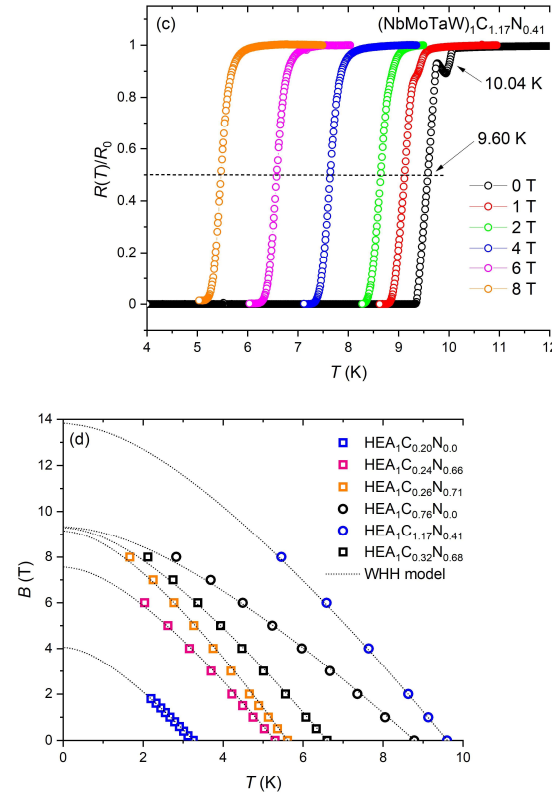


Figure 6. (a) - temperature dependencies of normalized resistance $R(T)/R_0$ for the $(\text{NbMoTaW})_1\text{C}_x\text{N}_y$ film of Series I with $x = 0.2$ and $y = 0.0$, (b) - of Series Ib with $x = 0.32$ and $y = 0.68$ and (c) - of Series II with $x = 1.17$ and $y = 0.41$ in increasing magnetic field. (d) - temperature dependencies of the upper critical field B_{c2} (symbols) for some of the $(\text{NbMoTaW})_1\text{C}_x\text{N}_y$ films together with corresponding fits based on the WHH model [41] (lines). The estimated $B_{c2}(0)$ values are listed in Table 1.

5. Conclusions

Transport and magnetization investigations of sputtered $(\text{NbMoTaW})_1\text{C}_x\text{N}_y$ carbonitride films show that the concentration of carbon plays the dominant role in the observed about threefold enhancement of the superconducting transition temperature T_c . This is probably related to the lower atomic mass of C compared to N that can lead to a phonon-frequency increase and to the parallel increase of the electron-phonon interaction due to different bonding of carbon atoms (compared to nitrogen) to the metallic sub-lattice. However, as the highest T_c values are observed at the verge of the *fcc* structure stability (for concentrations $y > 0.71$ and $x + y > 1.58$ two-phase structures begin to form), it indicates that the T_c enhancement is additionally related to the proximity of structural instability [34].

Further investigations will be needed, especially on high entropy carbonitrides in the form of bulk crystalline samples, from which it will be possible to determine exactly how the electronic density of states, the phonon modes and the electron-phonon interaction change with C and N incorporation, especially at their higher concentrations.

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