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# Structure and Phase Composition of V-Al-N-C Master Alloy

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## Abstract

The article presents the results of studying the phase composition and microstructure of the V-Al-N-C alloy, intended mainly for doping titanium alloys, but also of interest to manufacturers of structural steels. The V-Al-N-C alloy was obtained by the method of out-of-furnace aluminothermic smelting of a mixture containing vanadium pentoxide, aluminum powder, nitrided by the SHS method powdered V-Al-(17-20)N (wt.%) alloy and graphite in copper uncooled molds. The phase composition was determined by X-ray phase analysis (diffractometer - DRON-2.0, radiation - Cu-Kα, monochromator - graphite). The microstructure and composition of the phases were investigated by X-ray microanalysis using a JSM-59000LV scanning electron microscope (Japan) and an Oxford INCA Energy 200 energy-dispersive X-ray spectrometer (United Kingdom). It is revealed that the matrix of the V-Al-N-C alloy, containing (wt. %): 73.9 V; 23.7 Al, 1.2 N, 0.69 C, and 0.08 $O_2$, are represented by the solid solution of aluminum in vanadium. The main nitrogen-containing phase is aluminum nitride AlN of a cubic structure. The carbide phase can be identified as $V_2Al_{0.9}C_{1.1}$. Nitride and carbide phases are distributed quite uniformly in the alloy matrix. The carbide phase in the structure of the V-Al-N-C alloy is predominantly in the form of threadlike crystals up to 100 μm in length. The nitride phase is represented by small (up to 10 μm) and large (30 ÷ 100 $\mu$m) inclusions of irregular geometric shape with rounded and pointed edges forming conglomerates of branched irregular shapes, which are located around the aluminum oxide $Al_2O_3$.

**Keywords:** vanadium, aluminum, nitrogen, carbon, master alloys, structure, phase composition, nitrides, carbides

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## 1. Introduction

Titanium and alloys based on it have unique physicomechanical and corrosive properties and are widely used in the aerospace, chemical industries, in shipbuilding, mechanical engineering, automotive, biomedicine [1–9]. These properties of the alloys acquire due to the doping of titanium with elements that affect the temperature of its polymorphic transformation (α- and β-stabilizers), and neutral reinforcers, which are introduced into

the charge of smelting only in the form of master alloys. Carbon, oxygen, and nitrogen form introduction solid solutions with titanium. Like aluminum, they stabilize the α phase, increasing the transition temperature for ⇆ β. These elements are considered harmful impurities that deteriorate the ductility and viscosity of titanium alloys. However, their small amounts, especially oxygen and nitrogen, greatly increase the strength of titanium [10, 11]. The coefficient of titanium hardening by nitrogen is 20.0 - 25.0 MPa for every 0.01% N. Hardness, respectively, increases by HB 6.0. Every hundredth fraction of a percent for carbon increases the tensile strength of titanium by 7.0 - 10.0 MPa and hardness by HB 2.0. However, the content of nitrogen and carbon in titanium alloys, as a rule, should not exceed 0.05 and 0.20 wt. %, respectively [1, 10, 12–16].

The main producers of master alloys, based on rare refractory metals, for the titanium industry in the world are: JSC Uralredmet, Russia; Gesellschaft für Elektrometallurgie GmbH (GFE), Germany; Reading Alloys, USA; EVRAZ Stratcor, Inc./Kennametal International Specialty Alloys (ISA), USA. The production of the V-Al-N-C master alloy at Uralredmet, the main supplier of master alloys for VSMPO-AVISMA Corporation, began relatively recently. At present, work is underway to improve the smelting technology, search for optimal charge mixtures, develop new precursor nitrogen and carbon containing alloys in order to produce ingots with the equal distribution of alloying elements over their cross section and with an oxygen content not exceeding 0.1 wt. % [17]. The chemical composition of the V-Al-N-C master alloy for the major global manufacturers is given in Table 1.

Table 1: The chemical composition of the V-Al-N-C master alloy for various manufacturers.

| **Element** | **Composition, wt. %** | | |
|---|---|---|---|
| | **Uralredmet (Russia)** [17] | **Reading Alloys (USA)** [18] | **Evraz Stratcor/ Kennametal ISA (USA)** [19] |
| V | 70-76 | 72-77 | 73-78 |
| Al | 29-23 | 22-27 | 22-27 |
| N | 1.10-1.50 | 0.25-0.90 | ≤ 0.60 |
| S | < 0.010 | < 0.024 | < 0.025 |
| C | 0.6-0.9 | 0.250-0.900 | < 0.600 |
| P | < 0.020 | < 0.035 | < 0.030 |
| Si | < 0.300 | < 0.300 | < 0.350 |
| Fe | < 0.500 | < 0.450 | < 0.300 |
| O | < 0.100 | < 0.200 | < 0.200 |

Earlier [20–24], we studied the structure and phase composition of V-Al-N, Al-V-Ti-C and V-Al-Ti-N-(C) master alloys. This paper presents information on the phase composition and microstructure of the V-Al-N-C master alloy, which may be of interest not

only to manufacturers of titanium alloys but also to manufacturers of highly alloyed constructional steels.

## 2. Materials and Research Methods

The V-Al-N-C master alloy at JSC "Uralredmet" is produced by the method of out-of-furnace aluminothermic reduction of vanadium pentoxide [25–27]. Melting is carried out with the upper fuse of the mixture in uncooled copper molds. As a nitrogenizator, vanadium-alumina powder nitrated by the SHS (self-propagating high-temperature synthesis) method is used [28], and graphite is used as a carbidization agent. The chemical composition of the master alloy provided to us for research is given in Table 1. An ingot weighing 96.0 kg is melted from a mixture (184.5 kg) containing, in addition to the main components, about 17.0 wt. % of the recycled materials in the crumb form of the master alloy V-Al-N-C and 4.0 wt. % of fluxing additives (CaO, $CaF_2$).

X-ray phase analysis (XRPA) of four samples taken from the ingot of the master alloy according to the scheme shown in Figure 1, performed on an x-ray diffractometer DRON-2.0 with automatic programmed control (Cu-Kα radiation, angle range from 10 to 90, speed 1 deg/min).

The master alloy structure was studied by electron microprobe analysis EMPA using a JSM-59000LV scanning electron microscope (Japan) and an Oxford INCA Energy 200 energy-dispersive X-ray spectrometer (United Kingdom).

Table 2: The results of chemical analysis for the V-Al-N-C master alloy.

| Elements content, wt. % | | | | |
|---|---|---|---|---|
| V | Al | N | C | $O_2$ |
| 73.90 | 23.70 | 1.20 | 0.69 | 0.08 |

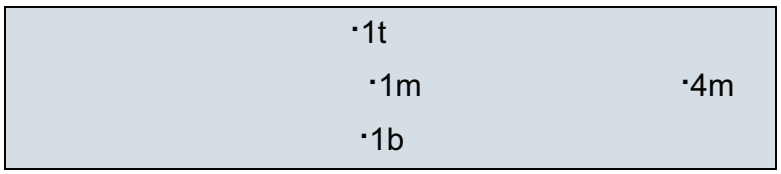



**Figure** 1: Sampling scheme from the master alloy V-Al-N-C ingot.

## 3. Results and Discussion

According to the results of XRPA (Figure 2), the V-Al-N-C master alloy matrix is a solid solution of aluminum in vanadium $V(Al)_{ss}$. The main nitrogen-containing phase is AlN

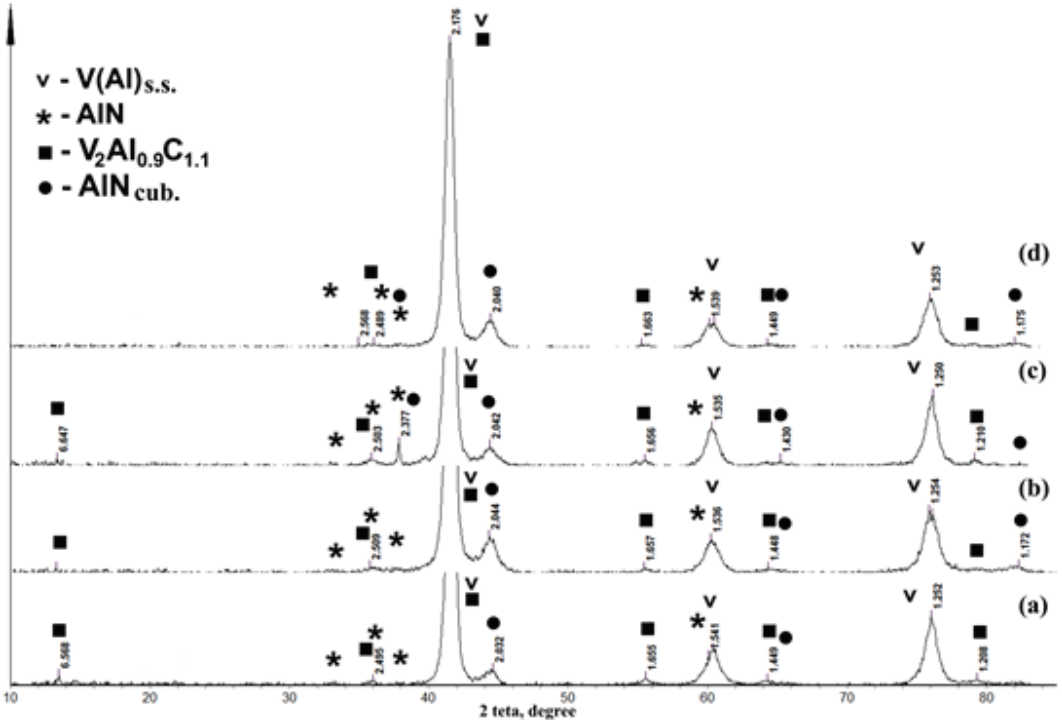
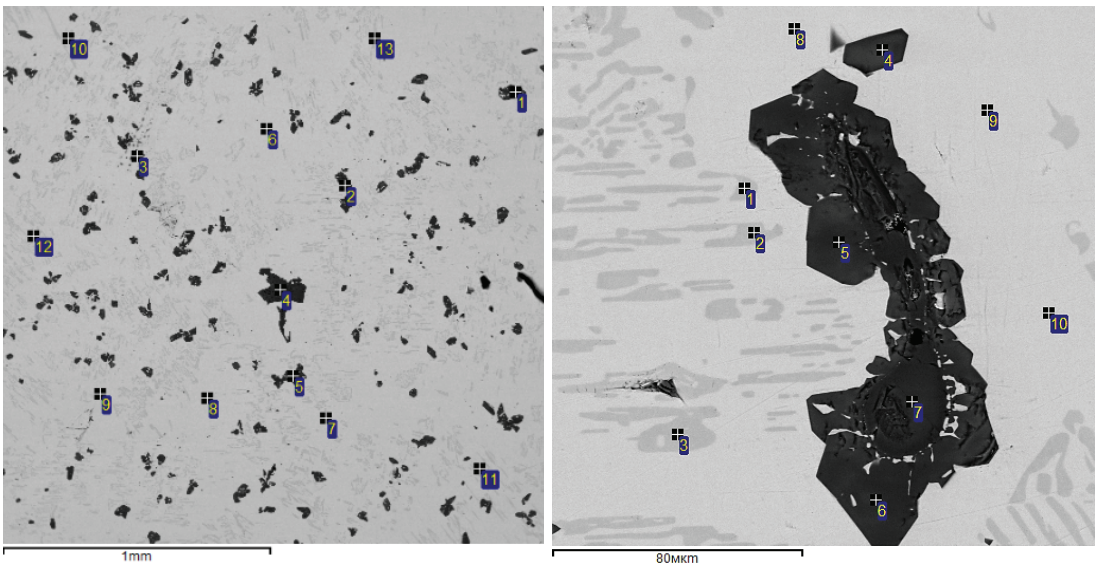



**Figure** 2: Diffraction patterns of samples from master alloys V-Al-N-C ingot: (a) – 1t; (b) – 1m; (c) – 1b; (d) – 4m (see scheme Figure 1).




(a) (b)

**Figure** 3: The image of the characteristic sections for the structure of the V-Al-N-C ingot in reflected electrons with the indication of the scanning points: (a) × 100; (b) × 1200.

of two modifications, with cubic type aluminum nitride prevailing. The carbide phase is identified by us as $V_2Al_{0.9}C_{1.1.}$Such a phase composition of the master alloy can be traced in all four samples.

Table 3: The composition of the master alloy V-Al-N-C phases.

| N°. of point | Element composition, at. % | | | | | | | Phase |
|---|---|---|---|---|---|---|---|---|
| | C | N | O | Al | Si | V | Fe | |
| Figure 3(a) | | | | | | | | |
| 1 | - | 49.95 | 1.61 | 47.67 | - | 0.77 | - | AlN+V(Al)$_{ss.}$ |
| 2 | - | 8.69 | 52.86 | 38.19 | - | 0.26 | - | $Al_2O_3$+AlN |
| 3 | - | 47.17 | 2.20 | 46.24 | - | 4.39 | - | $Al_2O_3$+V(Al)$_{ss.}$ |
| 4-5 | - | 48.48 | 2.68 | 48.57 | - | 0.22 | 0.05 | AlN+$Al_2O_3$ |
| 6-9 | - | - | - | 37.01 | 0.53 | 62.25 | 0.21 | Matrix V(Al)$_{ss.}$ |
| 10, 12, 13 | 25.90 | - | - | 24.13 | 0.08 | 49.89 | - | $V_2Al_{0.9}C_{1.1}$ |
| 11 | 31.15 | - | - | 21.41 | 2.34 | 45.10 | - | $V_2Al_{0.9}C_{1.1}$+SiC |
| Figure 3 (b) | | | | | | | | |
| 1-3 | 28.39 | - | - | 22.83 | - | 48.78 | - | $V_2Al_{0.9}C_{1.1}$ |
| 4-6 | - | 51.62 | 0.26 | 47.68 | - | 0.44 | - | AlN |
| 7 | - | 9.92 | 54.22 | 35.53 | 0.15 | 0.11 | - | $Al_2O_3$+AlN |
| 8-10 | - | - | - | 36.03 | 0.58 | 63.14 | 0.25 | Matrix V(Al)$_{ss.}$ |

The composition of the master alloys and inclusions was determined by the EMPA method. Typical sections of the structure with scanning points printed on them are shown in Figure 3. It can be seen from the figure that dark small (≤ 10 μm) and large (30 ÷ 100 μm) inclusions of irregular shape with rounded and acute-angled edges are present in the structure of the ingot. Large inclusions form branched conglomerates. In contrast to the V-Al-N master alloy [20, 21], gray areas up to 100 μm in length, mostly in the form of whisker crystals, are found in the structure of the V-Al-N-C master alloy.

According to the results of the EMPA (Table 3), the master alloy matrix (light gray area) is a solid solution of aluminum in vanadium. Dark inclusions of irregular geometric form and conglomerates formed from them are close in composition to stoichiometric aluminum nitride. As in the case of the V-Al-N master alloy, conglomerates are formed near the particles of aluminum oxide. Gray inclusions are ternary carbide $V_2Al_{0.9}C_{1.1}$, identified by us earlier during the samples study for the V-Al-N-C master alloy by XRPA method. Single inclusions, in which Al (≈ 40.0 at.%), N (up to 10.0 at.%) and O (the rest of it) were determined by the EMPA method, can be considered a mixture of $Al_2O_3$+AlN, rather than aluminum oxonitrides. Iron and silicon, most likely, were introduced during the manufacture of thin sections.

## 4. Conclusions

1. Using X-ray phase analysis and electron microprobe analysis EMPA, it was established that the phase composition of the V-A-N-C master alloy is a solid solution of aluminum in vanadium, in which nitride (AlN) and carbide ($V_2Al_{0.9}C_{1.1}$) inclusions are evenly distributed.

2. The carbide phase mainly has the form of whiskers up to 100 microns in length. Nitride phase is represented by small (up to 10 μm) and large (30 ÷ 100 μm) inclusions of an irregular geometric shape with rounded and pointed edges forming conglomerates of branched irregular shape. Conglomerates, in turn, are formed around $Al_2O_3$alumina.

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