

Thermodynamic simulation of the V-Al-N-C master alloy aluminothermic smelting

© Alexey V. Larionov,^{1*} Denis V. Taranov,¹
Vladimir M. Chumarev,¹ and Leonid A. Smirnov²

¹Laboratory of Pyrometallurgy of Nonferrous Metals. Institute of Metallurgy of the Ural Branch of the Russian Academy of Sciences. Amundsen St., 101. Ekaterinburg, 620016. Russia.

Phone: +7 (343) 232-91-82. E-mail: a.v.larionov@ya.ru

²Laboratory of Steel and Ferroalloys. Institute of Metallurgy of the Ural Branch of the Russian Academy of Sciences. Amundsen St., 101. Ekaterinburg, 620016. Russia.

Phone: +7 (343) 232-91-77. E-mail: uim@ural.ru

*Supervising author; [†]Corresponding author

Keywords: master alloy, vanadium, aluminum, nitrogen, carbon, V₂AlC, aluminum nitride, aluminothermy, thermodynamic simulation, phase formation.

Abstract

For microalloying of titanium with nitrogen and carbon, the V-Al-N-C complex master alloy is used. One of the main requirements presented by consumers of this ligature to its composition is oxygen content of less than 0.1 % mass. The use of elemental carbon (graphite) in the mixture for out-of-furnace aluminothermic smelting of the V-Al-N-C master alloy promotes the formation of aluminum oxonitrides in the melt, which, in the process of forming the metal and slag phases, can be stored in the alloy as separate inclusions. Since carbon in the master alloy is present in the form of V₂Al_{0.96}C_{1.1} carbide, it is advisable to replace graphite in the composition of the smelting mixture with an alternative precursor containing carbide of this composition. The paper presents the results of thermodynamic simulation of phase formation occurring in the process of V-Al-N-C master alloy smelting using various carbidizers. The equilibrium temperature dependences were obtained using the HSC Chemistry 6.12 software, the database of which was supplemented by the missing thermochemical characteristics of vanadium aluminides (VAl₃, V₅Al₈, V₃Al₂) and V₂AlC carbide borrowed from published sources. Thermodynamic models that take into account the formation of these intermetallic compounds adequately describe the processes that occur during the interaction of mixture components for the aluminothermic smelting of V-Al-N-C alloys. The predicted elemental and phase compositions of the V-Al-N-C model alloys are in a good agreement with the data of chemical, XRD and EMPA analyzes of samples of real alloys. Models that take into account the formation of V₂AlC carbide and vanadium aluminides are applicable for calculating the compositions and thermal stability of mixtures, as well as for predicting the V-Al-N-C alloys smelting products. From the point of view of thermodynamics, replacing graphite in a mixture of the V-Al-N-C master alloy smelting with a precursor alloy V(70)-Al(23)-C(7), carbon in which is represented as V₂AlC carbide and vanadium carbides V₂C and VC, will not affect the carbon distribution over its phase component and will not adversely affect the technological performance of the smelting.

References

- [1] S.G. Glazynov, V.N. Moiseev. Konstruktsionnyye titanovyie splavy. *Moscow: Metallurgiya*. **1974**. 368p. (russian)
- [2] I.V. Gorynin, B.B. Chechulin. Titan v mashinostroyeniye. *Moscow: Mashinostroyeniye*. **1990**. 400p. (russian)
- [3] C. Leyens, M. Peters. Titanium and Titanium Alloys. Fundamentals and Application. *WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim*. **2003**. 513p.
- [4] M.A. Khorev, A.I. Khorev. Titanovyie splavy, ikh primeneniye i perspektivy. *Materialovedeniye*. **2005**. No.7. P.25-34. (russian)
- [5] O.S. Oryshchenko, A.S. Kudryavtsev, V.I. Mikhaylov, V.P. Leonov. Titanovyie splavy dlya morskoy tekhniki i atomnoy energetiki. *Voprosy materialovedeniya*. **2011**. No.1. P 60-74. (russian)
- [6] T.V. Pavlova, O.S. Kashapov, N.A. Nochovnaya. Titanovyie splavy dlya gazoturbinnnykh dvigateley. *Vse materialy. Entsiklopedicheskiy spravochnik*. **2012**. No.5. P.8-14. (russian)

- [7] C. Veiga, J.P. Davim, A.J.R. Loureiro. Properties and applications of titanium alloys: A brief review. *Rev. Adv. Mater. Sci.* **2012**. Vol.32. P.133-148.
- [8] W. Florkiewicz, D. Malina, B. Tyliszczak, A. Sobczak-Kupiec. Manufacturing of Titanium and Its Alloys. In: G. Królczyk, M. Wzorek, A. Król, O. Kochan, J. Su, J. Kacprzyk (eds). Sustainable Production: Novel Trends in Energy, Environment and Material Systems. *Studies in Systems, Decision and Control. Springer, Cham.* **2020**. Vol.198. P.61-74.
- [9] I.I. Kornilov, P.B. Budberg. Tipy diagramm sostoyaniya troynykh sistem na osnove titana. *Dokl. AN SSSR.* **1958**. 119:5. P.942-944. (russian)
- [10] A.L. Andreyev, N.F. Anoshkin, K.M. Borzetsovskaya, G.A. Bochvar, S.G. Glazunov. Titanovyye splavy. Plavka i lit'ye titanovykh splavov. Pod redaktsiyey V.I. Dobatkina. *Moscow: Metallurgiya.* **1978**. 384p. (russian)
- [11] Ye.A. Borisova, G.A. Bochvar, M.YA. Brun, S.G. Glazunov, B.A. Kolachev, O.S. Korobov, A.V. Mal'kov, V.N. Moiseyev i dr. Titanovyye splavy. Metallografiya titanovykh splavov. Pod red. Glazunova S.G. i Kolacheva B.A. *Moscow: Metallurgiya.* **1980**. 464p. (russian)
- [12] A.A. Il'in, B.A. Kolachev, I.S. Pol'kin. Titanovyye splavy. Sostav, struktura, svoystva. Spravochnik. *Moscow: VILS-MATI.* **2009**. 520p. (russian)
- [13] <http://www.uralredmet.ru/sites/default/files/Master%20alloys%20for%20titanium%20alloys%20based%20on%20Vanadiumru.pdf>
- [14] *Pat. 2422246 Rossiyskaya Federatsiya, MPK B22F 3/23, C22C 29/16.* Sposob polucheniya azotsoderzhashchego materiala na osnove nitridov metallov dlya ligatur titanovykh splavov i azotsoderzhashchiy material dlya ligatur titanovykh splavov. Zakorzhevskiy V.V., Borovinskaya I.P., Dubrovskiy A.YA., Zelyanskiy A.V., Pazdnikov I.P., Chumarev V.M., zayavitel' i patentoobladatel' Uchrezhdeniye Rossiyskoy akademii nauk Institut strukturnoy makrokinetiki i problem materialovedeniya RAN (RU); zayavl. 25.03.2010; opubl. 27.06.2011, Byul. № 18.
- [15] M. Ish-Shalom. Formation of aluminum oxynitride by carbothermal reduction of aluminium oxide in nitrogen. *J. Mater. Sci. Lett.* **1982**. Vol.1. P.147-149.
- [16] N.D. Corbin. The influence of carbon, nitrogen and argon on aluminium oxynitride spinel formation. MSc thesis. *Massachusetts Institute of Technology, Cambridge, MA.* **1982**. P.37.
- [17] H.X. Willems, M.M.R.M. Hendrix, R. Metselaar, G. de With. Thermodynamics of Alon I: Stability at lower Temperatures. *J. Eur. Ceram. Soc.* **1992**. Vol.10. P.327-337.
- [18] H.X. Willems, M.M.R.M. Hendrix, R. Metselaar, G. de With. Thermodynamics of Alon II: Phase Relations. *J. Eur. Ceram. Soc.* **1992**. Vol.10. P.339-346.
- [19] A.N. Rylov, A.Yu. Raikov, A.V. Martynov, V.M. Chumarev, A.V. Larionov, N.I. Sel'menskikh. Use of Aluminum Nitride in Melting a V-Al-N Master Alloy. *Russian Metallurgy (Metally).* **2013**. Vol.4. No.7. P.477-481.
- [20] Roine A. HSC 6.0 Chemistry. Chemical reactions and Equilibrium software with extensive thermochemical database and Flowsheet simulation. *Pori: Outokumpu research Oy.* **2006**. 448p.
- [21] O. Kubashevskiy, K.B. Olkock. Metallurgicheskaya termokhimiya. Per. s angl. *Moscow: Metallurgiya.* **1982**. 392p. (russian)
- [22] L.Yu. Udoeva, V.M. Chumarev, A.V. Larionov, A.N. Rylov, M.V. Trubachev. Simulation of the Aluminothermic Smelting of Mo-Ti-Al and Mo-Ti-V-Cr-Al Alloys. *Russian Metallurgy (Metally).* **2013**. Vol.2013. No.8. P.564-569.
- [23] A.V. Larionov, V.M. Chumarev, L.Yu. Udoeva, A.N. Mansurova, A.N. Rylov, A.Yu. Raikov, A.P. Aleshin, M.V. Trubachev. Simulation of Aluminothermic Smelting of Al-Zr and Al-Zr-Mo-Sn Alloys. *Russian Metallurgy (Metally).* **2013**. Vol.2013. No.9. P.633-638.
- [24] S.N. Tyushnyakov, and Evgeny N. Selivanov. Thermodynamic simulation of zinc reduction from cooper-smelting slag. *Butlerov Communications.* **2015**. Vol.43. No.9. P.108-115. DOI: 10.37952/ROI-jbc-01/15-43-9-108
- [25] A.G. Upolovnikova, V.M. Chumarev, and L.Y. Udoeva. Thermodynamic modeling of phase formation during the oxidation of niobium aluminide. *Butlerov Communications.* **2015**. Vol.44. No.12. P.146-149. DOI: 10.37952/ROI-jbc-01/15-44-12-146
- [26] V.M. Chumarev, L.Yu. Udoeva, A.V. Larionov, S.A. Vohmentsev, and D.V. Taranov. Simulation of aluminothermic smelting of the carbon-containing ligature for titanium alloys. *Butlerov Communications.* **2017**. Vol.49. No.1. P.50-56. DOI: 10.37952/ROI-jbc-01/17-49-1-50
- [27] A.V. Larionov, V.M. Chumarev, L.Yu. Udoeva, D.V. Taranov, and S.A. Vohmentsev. Thermodynamic simulation of the Al-V-Ti-C master alloy aluminothermicmelting. *Butlerov Communications.* **2017**. Vol.49. No.1. P.43-49. DOI: 10.37952/ROI-jbc-01/17-49-1-43

- [28] A.V. Larionov, L.Y. Udoeva, and V.M. Chumarev. Thermodynamic simulation of oxidation process of the $\text{Mo}_{\text{ss}}\text{-Mo}_3\text{Si}$ hypoeutectic alloy, doped with yttrium. *Butlerov Communications*. **2019**. Vol.57. No.2. P.101-110. DOI: 10.37952/ROI-jbc-01/19-57-2-101
- [29] A.V. Larionov, L.Y. Udoeva, and V.M. Chumarev. Thermodynamic simulation of oxidation process of the $\text{Mo}_{\text{ss}}\text{-Mo}_3\text{Si}$ hypoeutectic alloy, doped with scandium or neodymium. *Butlerov Communications*. **2019**. Vol.57. No.2. P.90-100. DOI: 10.37952/ROI-jbc-01/19-57-2-90
- [30] Matthias T. Agne, Michel W. Barsoum. Enthalpy of formation and thermodynamic parameters of the MAX phase V_2AlC . *Journal of Alloys and Compounds*. **2016**. No.665. P.218-224.
- [31] D.V. Taranov, A.V. Larionov, V.M. Chumarev, L.A. Smirnov, M.V. Trubachev, S.A. Vohmentsev. "Structure and Phase Composition of V-Al-N-C Master Alloy" in Theoretical and practical conference with international participation and School for young scientists «FERROALLOYS: Development prospects of metallurgy and machine building based on completed Research and Development». *KnE Materials Science*. **2019**. P.118-125.
- [32] AA.s. 515821 SSSR, M.Kl.2 S 22 S 27/02. Ligatura. A.L. Bereslavskiy, V.M. Maksimov, I.A. Porunkov, V.P. Urt'yev, Ye.A. Larichkin, V.I. Mikhnevich, V.V. Tetyukhin, G.A. Bezrukov, A.I. Arsent'yev, I.F. Khodos (SSSR). - № 2038814/22-1; zayavl. 28.06.1974; opubl. 30.05.1976, Byul. No.20.
- [33] N.P. Lyakishev, YU.L. Pliner, G.F. Ignatenko, S.I. Lappo. Alyuminotermya. *Moscow: Metallurgiya*. **1978**. 424p. (russian)