Diagnostics of Metal Nanopowders Produced by Electrical Explosion of Wires

Olga Nazarenko and Yulia Amelkovich

Abstract The features of using standard physicochemical methods of analysis for determining the basic characteristics of metal nanopowders are discussed. The methods for the analysis of the shape and size of particles, the value of the specific surface area, the particle size distributions, and parameters of chemical activity of metal nanopowders are considered. The combination of these diagnostic characteristics makes it possible to predict the technical properties of metal nanopowders and evaluate their qualities for use in technology. The experimental results of diagnostics of aluminum and tungsten nanopowders produced by the electric explosion of wires are presented.

1 Introduction

The development of engineering and technology is characterized by the transition to objects of the nanometer range ($\leq$100 nm) to improve the physical, chemical, and mechanical characteristics of materials [1, 2]. Reducing the size of structural elements is one of the ways to impart qualitatively new properties to a substance, which allows a significant increase in product quality and an increase in the productivity of technological processes.

Nanopowders (NPs) can be obtained by various methods [3–5]. One of the promising methods for producing nanopowders is the electrical explosion of wires (EEW), which makes it possible to control the dispersed composition, physical, chemical, and other properties of the powders obtained [6–11]. The EEW process is characterized by a high energy density (>10^{14} W/s) and rapid heating (>10^7 K/s) of the metal wire to high temperature (>10^4 K) [6, 8]. The formation of nanodispersed

O. Nazarenko (✉) · Y. Amelkovich
Division for Testing and Diagnostics, National Research Tomsk Polytechnic University, 30 Lenin Avenue, Tomsk, Russia 634050
e-mail: olganaz@tpu.ru

Y. Amelkovich
e-mail: amely@tpu.ru

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particles during EEW occurs under highly nonequilibrium conditions. Due to the nonequilibrium conditions of production, electroexplosive NPs of metals have several unusual properties: after passivation, they are resistant to oxidation and sintering at room temperature and are characterized by high diffusion activity upon heating. The combination of unusual properties of electroexplosive NPs makes it possible to use them in the preparation of alloys and composite materials as additives that reduce the sintering temperature and reduce the interaction time, as reagents in the preparation of complex organic compounds and biologically active drugs, as modifiers of polymers for the preparation of functional materials, etc.

Metal NPs are metastable systems [8, 12, 13]. Even if NPs of metals are stored in an inert atmosphere, processes of recrystallization, diffusion sintering, diffusion of water reduction products, etc. occur simultaneously in them. The problems of the diagnostics of the metal NPs are associated with the instability of their properties and high reactivity, and difficulties arise in the interpretation of the results as well [14, 15]. The choice of diagnostic methods is not only a technical but also a theoretical problem. Diagnostic methods are necessary both for analysis of the properties of the nanomaterials, studying the effect of production conditions on their phase composition and structure, and for monitoring the characteristics of NPs as input raw materials in various nanotechnologies.

This work aims to substantiate the use of standard physicochemical methods of analysis and corresponding parameters for diagnostics of metal nanopowders. For testing, we selected aluminum (Al) and tungsten (W) nanopowders obtained by the electric explosion of wires in argon and nitrogen.

2 Experimental

Aluminum and tungsten NPs were produced on the installation UDP-4G. The operation of the installation is described in detail in [8, 16]. The conditions for the production of aluminum and tungsten NPs (d_w is the diameter of the wire, V is the charging voltage, e/e_s is the ratio of the specific energy input in the wire e to the sublimation energy of the wire material e_s, e_a/e_s is the ratio of the arc stage energy e_a to the sublimation energy of the wire material, kind of gas in the discharge chamber and pressure) and the characteristics of the dispersion of the obtained powders (S_{sp} is the specific surface area, $\bar{a}_s$ is the mean surface particle diameter) are presented in Table 1. The passivation with low oxidation by working gas +0.1 vol.% air was carried out after the production of the metal NPs to prevent their self-ignition after the contact with air.

The ohmic shunt and the S8-17 oscilloscope were used for current measurement. The voltage on the exploding wire was measured using the ohmic voltage divider. The phase composition of the final products was investigated by an X-ray diffractometer DRON-3.0 using CuKα-radiation. The size and shape of the particles were determined using a JSM-840 scanning electron microscope (SEM) and a Hitachi H-8100 transmission electron microscope (TEM). The reactivity of the powders was

Table 1 Electrical explosion conditions for aluminum and tungsten wires

Material of wire	d_w (mm)	V (kV)	e/e_s	e_a/e_s	Gas	P (Pa)	S_{sp} (m^2/g)	$\bar{a}_s$ (nm)
Al	0.35	24	1.5	0.4	Ar	1.5×10^5	12	120
W	0.2	22	1.1	0.5	Ar	1.5×10^5	3.9	79
W	0.3	23	0.4	1.1	N_2	1.5×10^5	1.9	164
W	0.3	23	0.7	0.8	N_2	1.5×10^5	1.7	183
W	0.3	23	0.4	0.9	N_2	0.3×10^5	2.6	120

investigated using an SDT Q600 thermal analyzer. The thermal analysis was carried out in a linear heating mode from 20 to 1000 °C at a heating rate of 10 °C/min in an air atmosphere. The particle size distributions were analyzed by the laser diffraction technique using a Malvern Mastersizer.

3 Results and Discussion

3.1 Disperse Composition and Particle Size Distribution

Disperse composition of powders is one of the most important parameters that determine their technical characteristics (bulk density, flowability, reactivity, etc.), and, consequently, the field of application. With an increase in the dispersion of metal NPs (with a decrease in the particle size below 100 nm), their activity increases [17, 18], but the content of metals in the particles also decreases. Powder particles obtained by the EEW method, as a rule, have a spherical shape, and the powders themselves are polydisperse systems. The particle size of electroexplosive NPs varies in a wide range: from 5×10^{-9} to 10^{-3} m. The production of metal NPs with a size less than 30 nm is inexpedient due to the low sintering temperature, instability to oxidation during passivation and agglomeration. In inert media, powders with a size less than 30 nm are sintered by a diffusion mechanism, and in chemically active media, they interact with an explosion. Therefore, the problem of finding the conditions for obtaining nanopowders that provide a high dispersion and narrow particle size distribution in the range of 30–60 nm is relevant and directly related to the problem of diagnostics of the disperse composition of NPs.

According to the SEM images, the aluminum NP consists of the particles with a diameter of ~100 nm (Fig. 1a) but it also contains the particles of both a larger diameter ~200 nm and a smaller diameter ~50 to 60 nm. The shape of the particles is close to spherical; there are separate agglomerates of particles that are partially sintered. Tungsten nanoparticles also have a shape close to spherical with a smooth surface [19, 20]. Figure 1b shows the SEM image of sample 3 from Table 1. It can be seen that most of the particles have a diameter of less than 100 nm.

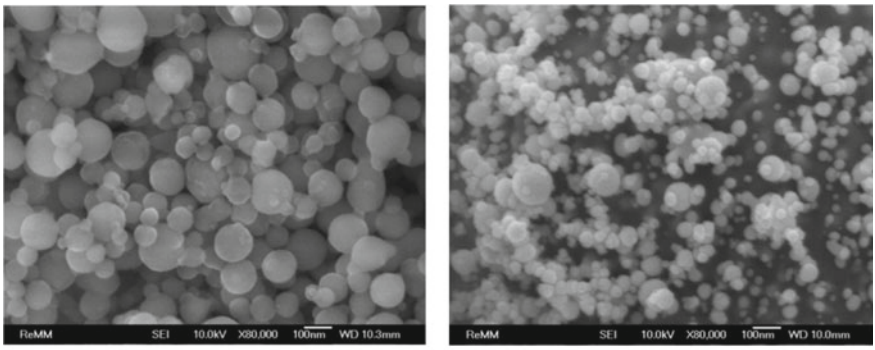

Fig. 1 SEM images of aluminum **a** and tungsten **b** nanopowders

Figure 2a shows a TEM image of the aluminum nanoparticle. The aluminum nanoparticle consists of a metal core and an outer shell [16]. During the formation of nanoparticles under highly non-equilibrium conditions typical for EEW, a redistribution of impurities occurs in the surface layers and near-surface layers. In the process of cooling aluminum nanoparticles, refractory impurities, which were initially contained in the original wire (Fe, Mn, Cu), are concentrated in the near-surface layers. When the powders are passivated by slow oxidation of air, the gas-medium is desorbed, the air components are adsorbed, and a protective oxide-hydroxide layer is formed. Unlike coarse powders, the thickness of oxide-hydroxide layers on the metal nanoparticles ranges from 2 to 8 nm. Moreover, with a decrease in the particle diameter from 100 to 50 nm, the thickness of oxide-hydroxide layers decreases.

Figure 2b shows a TEM image of the tungsten nanoparticle (sample 2, Table 1).

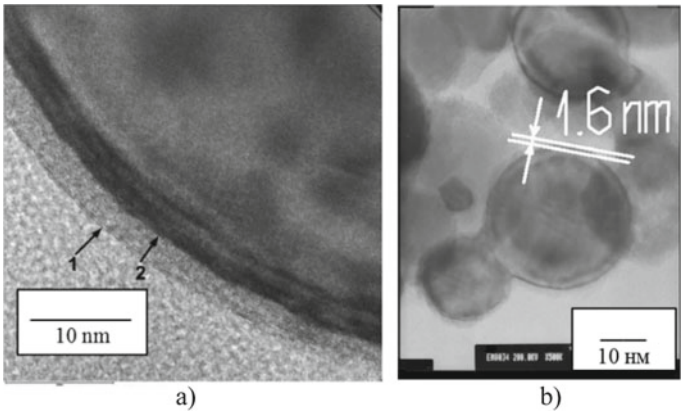

Fig. 2 TEM images of aluminum **a** and tungsten **b** nanopowders

The thickness of the oxide layer on the tungsten nanoparticle is 1.6 nm [21, 22]. At such a thickness, the oxide layers are X-ray amorphous, which makes it difficult to determine their phase composition using X-ray phase analysis.

All electroexplosive powders are characterized by a three-modal particle size distribution, which is associated with the mechanism of destruction of the wires in the process of EEW and subsequent cooling of the primary products of the EEW [3, 16, 19]. Figure 3 shows the graphs of the particle size distribution for the tungsten NPs obtained by EEW.

The graphs of the particle size distribution make it possible to judge the effect of production conditions on the disperse composition of powders. When replacing the working gas from argon to nitrogen at a pressure of 1.5×10^5 Pa, the particle diameter corresponding to the first maximum on the distribution curve decreases from 0.686 to 0.169 μm, and the average particle diameter decreases from 2.404 to 0.694 μm (Fig. 3a, b). When using nitrogen as working gas, with a decrease in pressure from 1.5×10^5 to 0.3×10^5 Pa, the particle diameter corresponding to the first maximum did not change and was 0.169 μm, but the average particle diameter

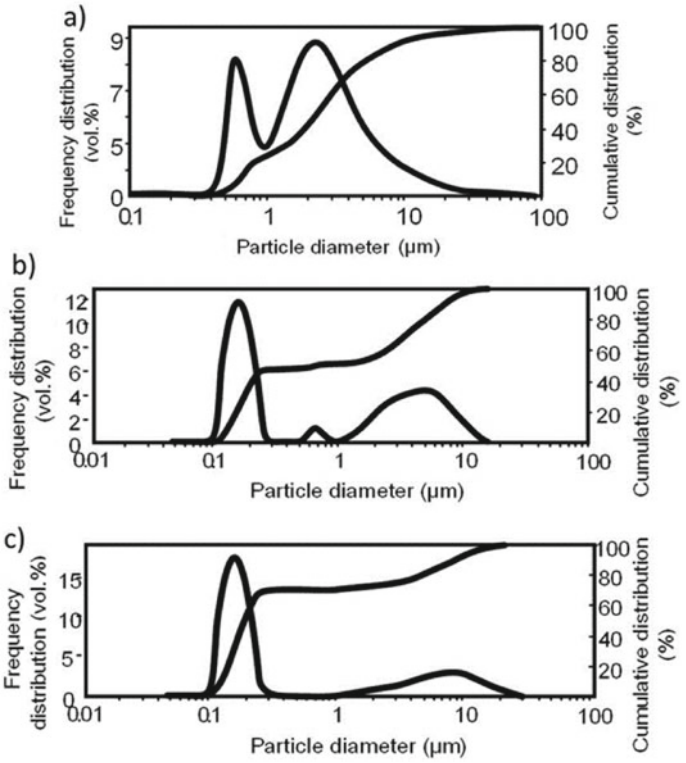

Fig. 3 Particle size distribution of tungsten nanopowders produced in **a** Ar, $P = 1.5 \times 10^5$ Pa, **b** N_2, $P = 1.5 \times 10^5$ Pa, **c** N_2, $P = 0.3 \times 10^5$ Pa

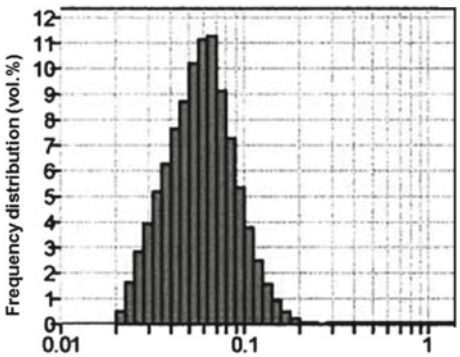

Fig. 4 Particle size distribution of tungsten nanopowder

in the powder decreases from 0.694 to 0.196 μm (Fig. 3b, c). The number of particles corresponding to the first maximum on the distribution curve increases accordingly.

It should be noted that there are no nanodispersed particles in the particle size distribution plots. This is explained by the peculiarities of the formation of electrical explosion products: in the process of the scattering of the wire destruction products, agglomerates are formed, the presence of which introduced an error in the measurements of the particle size of the powder by the laser diffraction technique. At the same time, electron microscopic studies (Fig. 2b) showed the presence of particles of the nanodispersed range. These results indicate the need for preliminary preparation of powders for the destruction of particle aggregates before analysis. The tungsten NP (sample 2, Table 1) was previously suspended in ethanol and sonicated (200 W, 22 kHz) for 15 min before analysis to determine the particle size distribution. According to the results obtained (Fig. 4), the tungsten NP has a relatively narrow particle size distribution in the range of 0.02–0.2 μm with a maximum of 0.06 μm [21, 22].

3.2 Reactivity Parameters

Differential thermal analysis (DTA) is used to test the stability of nanopowders and their mixtures to oxidation and chemical interaction [23–28]. Based on the DTA data, four parameters of chemical activity are determined. The parameters of the chemical activity of metal nanopowders are understood as the following values [24, 26]:

1. The temperature of oxidation onset t_o (°C) characterizes the thermal stability of nanopowders in the air; it is defined as the temperature at which an increase in the sample mass begins.
2. The maximum oxidation rate v_{max} (mg/s) characterizes the intensity/rate of weight gain and heat release during oxidation.

3. The degree of oxidation α (%) is determined for a given temperature range and characterizes the degree of conversion of the initial nanopowder into oxidation products.
4. Specific thermal effect or specific heat release ΔH (J/g) defines the amount of the heat released normalized to the mass of the nanopowder.

The practice has shown that the use of weighed portions of NPs of active metals, for example, aluminum, over 50 mg during DTA, led to combustion or melting of the crucible, combustion of the holder, and other undesirable effects. To reduce the thermal effects during the oxidation of nanopowders in air, it was recommended to use small weighed amounts of powders less than 10 mg.

According to DTA, when heated in air, aluminum NP is highly active (Fig. 5). The desorption of gaseous substances adsorbed on the surface of particles (~3 wt%) at the beginning of the heating is noticeable in the thermogravimetric (TG) curve. Then, there is a sharp increase in the rate of mass growth with a maximum at 630 °C (TG) and the release of heat (DTA).

The oxidation process of tungsten powders included three stages [19]. The presence of two maxima of heat release is associated with the polymodal particle size distribution: in the first place, the fraction of smaller particles is oxidized, and then the larger fraction is oxidized. Thermal activity parameters closely correlate with the dispersion of the studied powders and with the conditions for their preparation.

The parameters of the chemical activity of the studied aluminum and tungsten NPs, necessary for assessing the oxidation resistance, were determined from the data of thermal analysis and are presented in Table 2.

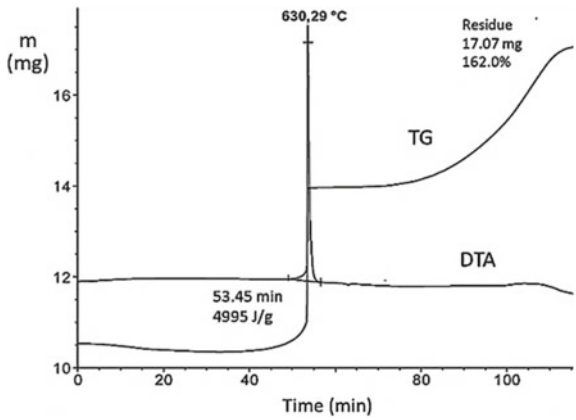

Fig. 5 TG–DTA curves of aluminum nanopowder, m = 5 mg

Table 2 Parameters of chemical activity of aluminum and tungsten nanopowders

Sample	t_o (°C)	α (%)	v_{max} (%/s)	ΔH (J/g)
Al	450	63.8	0.13	4995
W	370	24.1	0.03	3197

4 Conclusion

The possibility and some features of using standard physicochemical methods of analysis for the diagnostic of metal nanopowders are shown by the example of the analysis of aluminum and tungsten nanopowders obtained by the method of the electrical explosion of wires. The following methods were taken into consideration: the method of low-temperature adsorption of nitrogen, the method for determining the particle size distribution, electron microscopy, and thermal analysis. As a result of the application of these methods, metal nanopowders were characterized by the following characteristics: nanostructural characteristics (particle shape, size, particle surface condition, and specific surface area), particle size distribution, and parameters of chemical activity. The combination of these diagnostic features makes it possible to predict the technical characteristics of metal nanopowders and to select the powders of the required quality for use in nanotechnology.

References

1. Gogotsi, Y.: Nanomaterials Handbook. CRC Press, Boca Raton (2006)
2. Jeevanandam, J., Barhoum, A., Chan, Y.S., et al.: Review on nanoparticles and nanostructured materials: history, sources, toxicity and regulations. Beilstein J. Nanotechnol. **9**(1), 1050–1074 (2018). https://doi.org/10.3762/bjnano.9.98
3. Wang, Y., Xia, Y.: Bottom-up and top-down approaches to the synthesis of monodispersed spherical colloids of low melting-point metals. Nano Lett. **4**(10), 2047–2050 (2004). https://doi.org/10.1021/nl048689j
4. Bozon-Verduraz, F., Fiévet, F., Piquemal, J.-Y., et al.: Nanoparticles of metal and metal oxides: some peculiar synthesis methods, size and shape control, application to catalysts preparation. Braz. J. Phys. **39**(1A), 134–140 (2009). https://doi.org/10.1590/S0103-97332009000200002
5. Khan, I., Saeed, K., Khan, I.: Nanoparticles: properties, applications and toxicities. Arab. J. Chem. **12**(7), 908–931 (2019). https://doi.org/10.1016/j.arabjc.2017.05.011
6. Kwon, Y.S., Jung, Y.H., Yavorovsky, N.A., et al.: Ultra-fine powder by wire explosion method. Scr. Mater. **44**(8–9), 2247–2251 (2001). https://doi.org/10.1016/S1359-6462(01)00757-6
7. Kotov, Y.A.: The electrical explosion of wire: a method for the synthesis of weakly aggregated nanopowders. Nanotechnol. Russia **4**, 415–424 (2009)
8. Nazarenko, O.B., Gromov, A.A., Il'in, A.P. et al.: Electroexplosive nanometals. In: Gromov, A.A., Teipel, U. (eds.) Metal Nanopowders: Production, Characterization, and Energetic Applications, pp. 67–78. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim (2014)
9. Abdelkader, E.M., Jellis, P.A., Buckner, S.W.: Metal and metal carbide nanoparticle synthesis using electrical explosion of wires coupled with epoxide polymerization capping. Inorg. Chem. **54**(12), 5897–5906 (2015). https://doi.org/10.1021/acs.inorgchem.5b00697
10. Lerner, M.I., Glazkova, E.A., Lozhkomoev, A.S., et al.: Synthesis of Al nanoparticles and Al/AlN composite nanoparticles by electrical explosion of aluminum wires in argon and nitrogen. Powder Technol. **295**, 307–314 (2016)
11. Lázár, K., Varga, L.K., Kis, V.K., et al.: Electric explosion of steel wires for production of nanoparticles: reactions with the liquid media. J. Alloy. Compd. **763**, 759–770 (2018). https://doi.org/10.1016/j.jallcom.2018.05.32
12. Ivanov, G.V., Tepper, F.: "Activated" aluminum as a stored energy source for propellants. Int. J. Energetic Mater. Chem. Propul. **4**(1–6), 636–645 (1997)
13. Blackman, J.: Metallic Nanoparticles, Vol. 5, 1st ed. Elsevier, Oxford (2009)

14. Shuvalov, G.V., Klekovkin, I.V., Ilyin, A.P. et al: Scientific research on nanopowders diagnostics. In: Proceedings of the 6th International Forum on Strategic Technology (IFOST-2011), 49–51 (2011). https://doi.org/10.1109/IFOST.2011.6020962
15. Mourdikoudis, S., Pallares, R.M., Thanh, N.T.K.: Characterization techniques for nanoparticles: comparison and complementarity upon studying nanoparticle properties. Nanoscale **10**, 12871–12934 (2018). https://doi.org/10.1039/c8nr02278j
16. Kwon, Y.-S., Kim, J.-C., Ilyin, A.P., et al.: Electroexplosive technology of nanopowders production: current status and future prospects. J. Korean Powder Metall. Inst. **19**(1), 40–48 (2012)
17. Kwon, Y.S., Gromov, A.A., Ilyin, A.P., et al.: Passivation process for superfine aluminum powders obtained by electrical explosion of wires. Appl. Surf. Sci. **211**(1–4), 57–67 (2003). https://doi.org/10.1016/S0169-4332(03)00059-X
18. Gromov, A.A., Il'in, A.P., Teipel, U. et al.: Passivation of metal nanopowders. In: Gromov, A.A., Teipel, U. (eds.) Metal Nanopowders: Production, Characterization, and Energetic Applications, pp. 133–152. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim (2014)
19. Kwon, Y.-S., Kim, J.-C., Ilyin, A.P., et al.: Effect of electrical parameters and surrounding gas on the electroexplosive tungsten nanopowders characteristics. J. Korean Powder Metall. Inst. **19**(1), 49–54 (2012)
20. Ilyin, A.P., Nazarenko, O.B., Tikhonov, D.V.: Production of tungsten powders by electrical explosion of wires. J. Optoelectron. Adv. M. **10**(3), 645–648 (2008)
21. Gromov, A.A., Kwon, Y.S., Il'in, A.P., et al.: Specific features of the oxidation of a tungsten nanopowder. Russ. J. Phys. Chem. A **78**(9), 1484–1487 (2004)
22. Kwon, Y.S., Gromov, A.A., Ilyin, A.P., et al.: Features of passivation, oxidation and combustion of tungsten nanopowders by air. Int. J. Refract. Hard. Met. **22**(6), 235–241 (2004). https://doi.org/10.1016/j.ijrmhm.2004.06.005
23. Kwok, Q.S.M., Fouchard, R.C., Turcotte, A.M., et al.: Characterization of aluminum nanopowder compositions. Propell. Explos. Pyrotech. **27**(4), 229–240 (2002)
24. Gromov, A., Ilyin, A., An, V. et al.: Characterization of aluminum powders: I. Parameters of reactivity of aluminum powders. Propell. Explos. Pyrotech. **27**(6), 361–364 (2002)
25. Kwon, Y.S., Moon, J.S., Ilyin, A.P., et al.: Estimation of the reactivity of aluminum superfine powders for energetic applications. Combust. Sci. Tech. **176**(2), 277–288 (2004). https://doi.org/10.1080/00102200490255992
26. Gromov, A., Ilyin, A.: Characterization of aluminum powders: II. Aluminum nanopowders passivated by non-inert coatings. Propell. Explos. Pyrotech. **31**(5) 401–409 (2006)
27. Dilmukhambetov, E., Espolov, T., Ospanova, M., et al.: Reactivity to oxidation of metal nanopowders after electron irradiation. J. Mater. Sci. **2**(1), 175–181 (2013)
28. Sun, Y., Sun, R., Zhu, B., et al.: Thermal reaction mechanisms of nano- and micro-scale aluminum powders in carbon dioxide at low heating rate. J. Therm. Anal. Calorim. **124**(3), 1727–1734 (2016). https://doi.org/10.1007/s10973-016-5284-2