

ARCHIVES
of
FOUNDRY ENGINEERING

ISSN (2299-2944)
Volume 18
Issue 2/2018

11 – 14

DOI: 10.24425/122494

2/2



Published quarterly as the organ of the Foundry Commission of the Polish Academy of Sciences

Nonmetallic Inclusions in a New Alloy for Single-Crystal Permanent Magnets

I.V. Belyaev^a, V.E. Bazhenov^{b, *}, A.V. Kireev^a, A.V. Moiseev

^a Department of functional and constructional materials,

Vladimir State University named after A.G. and N.G. Stoletovs, Vladimir, Russia

^b National University of Science and Technology "MISiS", Leninskiy pr. 4, 119049 Moscow, Russia

^c Research and Production Association "Magnetron", Vladimir, Russia

* Corresponding author. E-mail address: V.E.Bagenov@gmail.com

Received 01.01.2018; accepted in revised form 20.02.2018

Abstract

The morphology, chemical composition and formation mechanism of non-metallic inclusions in magnetic alloy of Fe-Co-Ni-Cu-Al-Ti-Hf system were investigated. These alloys are used in manufacturing single-crystal permanent magnets. Modern methods for the identification of non-metallic inclusions, as well as computer simulation of the processes of their formation by Thermo Calc software were used in the work. It was found that studied alloy contains (Ti, Hf)S titanium and hafnium sulfides, (Ti, Hf)₂SC titanium and hafnium carbosulfides, Ti₂O₂S titanium oxisulfide, HfO₂ hafnium oxide, and Al₂O₃ aluminum oxide. No titanium and hafnium nitrides were found in the alloy. The bulk of nonmetallic inclusions are (Ti, Hf)₂SC carbosulfides and (Ti, Hf)S sulfides. All carbides and many oxides are within carbosulfides and sulfides. When the sulfur content in the alloy is no more than 0.2%, and carbon content does not exceed 0.03%, carbosulfides are formed in the solidification range of the alloy and has an faceted compact form. If the sulfur content in the alloy becomes more than 0.2% and carbon content more than 0.03%, the carbosulfide formation begins before the alloy solidification or at the beginning stages of solidification. In this case, carbosulfides are dendritic and coarse. Such carbosulfides actively float in the solidified melt and often come to the surface of the castings. In this case, specific surface defects are formed in single-crystal magnets, which are called sulfide stains. All titanium and hafnium sulfides are formed at the lower part of solidification range and have elongated shape.

Keywords: Magnetic alloys, Single-crystals, Non-metallic inclusions, Identification, Formation mechanism

1. Introduction

Fe-Co-Ni-Cu-Al-Ti-Hf alloys show promise as materials for manufacturing single crystal permanent magnets. These alloys exhibit the high potential ability to form the single crystal structure during unidirectional solidification. Permanent magnets made from these alloys have the highest magnetic properties and performance among the magnetic materials of this class: remnant induction $B_r = 1.15$ T, coercive force $H_{cb} = 135$ kA/m, maximum energy product $(BH)_{max} = 105$ kJ/m³, temperature coefficient of induction TCI = 0.0005 %/°C. For comparison, the best magnets produced from the

alloys of the Fe-Co-Ni-Cu-Al-Ti system have $B_r = 1.1$ T, $H_{cb} = 120$ kA/m, $(BH)_{max} = 88$ kJ/m³, TCI = 0.0005 %/°C [1, 2, 4]. Non-metallic inclusions substantially affect the structure, physical and technological properties, and performance of the products made from these alloys, namely, permanent magnets. In the literature there is data about nonmetallic inclusions present in magnetic alloys of the Fe-Co-Ni-Cu-Al-Ti system. These are TiS titanium sulfides, TiSCO titanium oxycarbosulfides, TiC titanium carbides, TiN titanium nitrides, TiCN titanium carbonitrides, Al₂O₃ aluminum oxides. Carbides, nitrides and oxides reduce the mechanical properties of these alloys and prevent the formation of single-crystal structure in castings obtained by directional

solidification technique. Sulfide inclusions, on the contrary, improve the mechanical properties of these magnetic alloys, and their formation promotes the growth of single-crystal structure in castings. All type of nonmetallic inclusions reduces the magnetic properties of permanent magnets [3-7]. No articles devoted to the study nonmetallic inclusions in Fe-Co-Ni-Cu-Al-Ti-Hf alloys are available.

The purpose of this work is to identify all non-metallic inclusions present in the Fe-Co-Ni-Cu-Al-Ti-Hf alloys used for manufacturing single-crystal permanent magnets and to study their formation mechanisms.

2. Materials and methods

For the investigation, we used single-crystal work pieces having the following chemical composition: Co-33.06%, Ni-13.8%, Cu-3.84%, Al-8.87%, Ti-5.02%, Hf-0.57%, and iron - balance (from herein, the contents are given in wt. %). The alloys also contain sulfur and carbon. In some samples, the sulfur and carbon contents were 0.12 and 0.02%, respectively; other alloys contain 0.32% S and 0.05% C.

Alloys were melted in an argon atmosphere using a vacuum induction furnace and a corundum crucible. As charge components, pure metals of high grades were used. Polycrystalline blanks of growing single crystals were obtained by pouring the melt in a ceramic mold. Single crystals were grown in an argon atmosphere by Bridgman method using a «Crystallizator-203 M» vacuum furnace. The chemical composition of the alloy was studied by X-ray fluorescence analysis using a standard-free ARL ADVANT X (USA) spectrometer. The sulfur and carbon contents in the alloy were determined using an ELTRA CS-800 (Germany) analyzer. Metallographic studies were carried out using a Tescan Vega 3 SBH (Czech Republic) scanning electron microscope equipped with an EDS analysis system Oxford (USA). Phase equilibria were calculated by CALPHAD method using Thermo-Calc software and a thermodynamic database TCFE7.

3. Results and discussion

It was found experimentally that the following non-metallic inclusions are present in the tested alloys: (Ti, Hf)S hafnium and titanium sulfides; (Ti, Hf)₂SC titanium and hafnium carbo-sulfides; Ti₂O₂S titanium oxysulfides; HfO hafnium oxide; Al₂O₃ aluminum oxide, (Ti, Hf) SCO titanium and hafnium carboxysulfides.

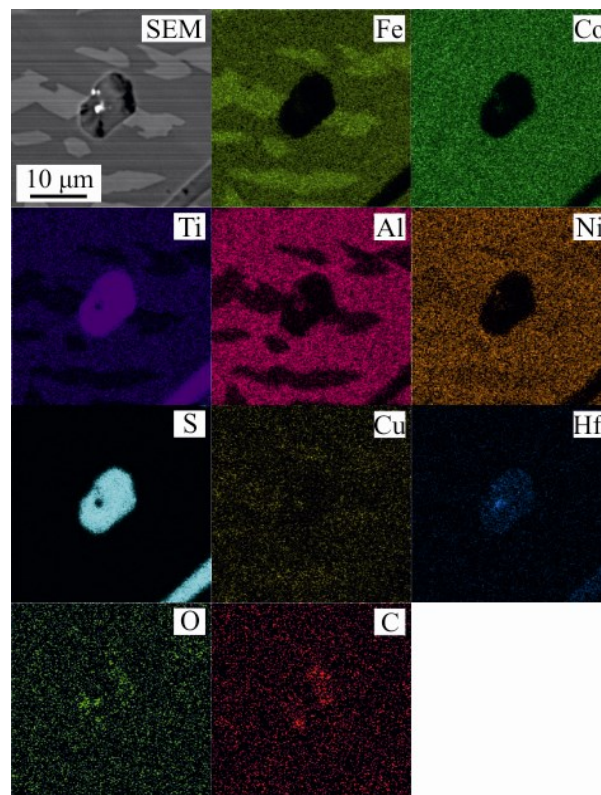


Fig. 1. Typical carbo-sulfide (Ti, Hf)₂SC with faceted compact shape (SEM image) and element distribution obtained by EDS: Fe, Co, Ti, Al, Ni, S, Cu, Hf, O, C

The majority of nonmetallic inclusions are the (Ti, Hf)₂SC carbo-sulfide, which are similar to those observed in [9-11]. When the sulfur and carbon contents in the alloy are 0.12 and 0.02%, respectively, carbo-sulfides form in the alloy solidification range. Formed carbo-sulfides have faceted compact shape and are relatively uniformly distributed in the alloy microstructure. Figure 1 shows the typical carbo-sulfide.

Calculation of phase equilibria in the alloy using Thermo-Calc allowed us to find that, at a sulfur content of more than 0.2% and a carbon content of more than 0.03%, the formation of carbo-sulfide starts in the beginning stages of alloy solidification. When the sulfur and carbon contents in the alloy are 0.32 and 0.05%, respectively, the carbo-sulfide formation starts before the onset of solidification. In this case, (Ti, Hf)₂SC carbo-sulfide inclusions are large and dendritic (Fig. 2). Such a carbo-sulfide inclusion actively floats in the solidified melt and often come to the surface of single-crystal casting. In this case, specific defects — sulfide stains appear on the surface of single-crystal magnets.

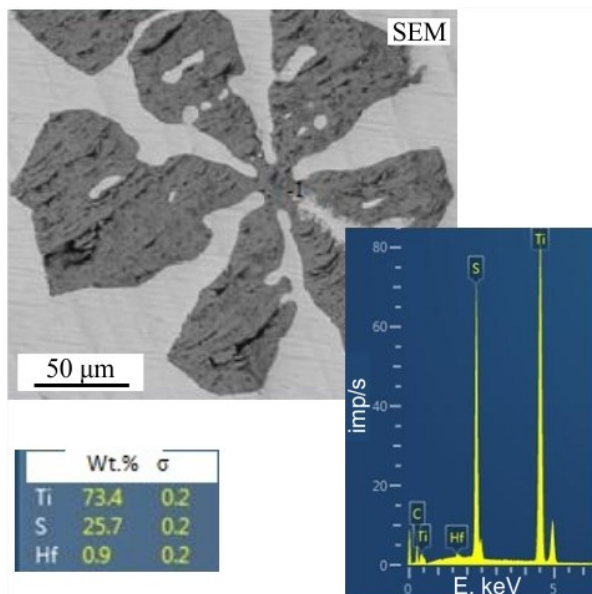


Fig. 2. Dendritic carbosulfide (Ti, Hf)₂SC (SEM image) and its chemical composition

The chemical composition of carbosulfide and sulfides of titanium and hafnium is given in Table. 1. The results showed that all titanium and hafnium sulfides are formed at the lower portions of solidification range and are elongated in shape. Hafnium is nonuniformly distributed within sulfide inclusions and tends to the inclusion boundaries. Typical (Ti, Hf)S sulfide is shown in Figure 3.

Table 1.

Composition of (Ti, Hf)₂SC carbosulfide and (Ti, Hf)S sulfide (EDS data)

Sulfide	Element content / wt.%			
	Ti	Hf	S	C
(Ti, Hf) ₂ SC	55.4–	2.8–	21.0–	12.0–
	60.7	8.4	22.0	12.7
(Ti, Hf)S	44.2–	12.4–	34.4–	4.6–
	44.4	12.7	35.2	4.9

Identification of the (Ti,Hf)₂SC inclusion was carried out by the EBSD method. This phase has a hexagonal close packed structure with lattice parameters $a = b = 3.21 \text{ \AA}$ (space group $6/mmm$). The data were obtained at an average angular deviation of 0.7.

Majority of carbosulfides and sulfides are complex inclusions and incorporate other inclusions, which are identified to be oxides or carbides. Hafnium oxide often is found in the form of individual inclusions. (Ti, Hf)SCO titanium and hafnium carboxysulfides are present exclusively within (Ti, Hf)₂SC carbosulfides. No titanium and hafnium nitrides were found in the alloy.

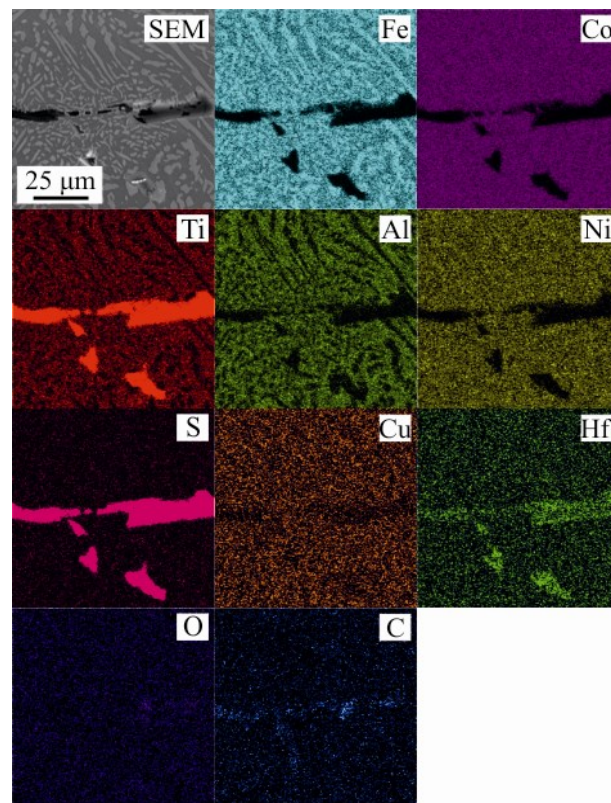
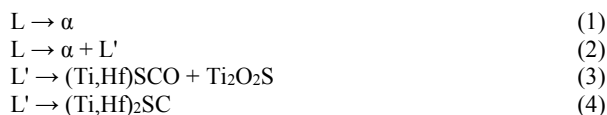


Fig. 3. Typical sulfide (Ti, Hf)S (SEM image) and element distribution obtained by EDS: Fe, Co, Ti, Al, Ni, S, Cu, Hf, O, C

Carbosulfides and sulfides have different mechanisms of formation. It has been established that carbosulfides (Ti,Hf)₂SC in alloys with a S = 0.2% and C = 0.03% content appear during solidification of the high-sulfur liquid L'. This transformation occurs between the liquidus temperature and the middle of the alloy solidification range. The high-sulfur liquid L' is formed as a result of the monotectic transformation $L \rightarrow \alpha + L'$ in the upper part of the alloy solidification range. The particles (Ti,Hf)SCO and Ti₂O₂S found inside the carbosulfides (Ti,Hf)₂SC are also formed as a result of high-sulfur monotectic liquid L' solidification. Their formation occurs, probably, before the formation of (Ti,Hf)₂SC. Thus, the sequence of reactions leading to the formation of these complex inclusions is as follows:



Here L is the liquid in the Fe-Co-Ni-Cu-Al-Ti-Hf system; L' is a high-sulfur monotectic liquid formed as a result of the monotectic transformation (2) and L' make miscibility gap with L.

The formation of carbosulfides (Ti,Hf)₂SC in an alloy with a content of S = 0.32%, C = 0.06% occurs as follows. At a temperature above the alloy liquidus, the melt decomposes into two immiscible liquids by the $L \rightarrow L' + L''$ transformation. One of these liquids named L', is enriched in sulfur and carbon. Drops of this

liquid have the ability to float in the melt and coagulate. As the temperature is lowered, these drops of liquid L' solidify according to the reactions (3) and (4). As a result, complex carbo-sulfides (Ti,Hf)₂SC are formed, having a dendritic shape and large dimensions.

Sulfides (Ti, Hf)S in the alloys of the Fe-Co-Ni-Cu-Al-Ti-Hf system are formed after finishing of the complex carbo-sulfide (Ti,Hf)₂SC formation reaction. The formation of these inclusions occurs in the lower part of the solidification range, probably due to the eutectic transformation, in analogy with the Fe-Ti-S-C and Fe-Co-Ni-Cu-Al-Ti system alloys [4, 8].

4. Conclusions

It was found that studied magnetically hard alloy of the Fe-Co-Ni-Cu-Al-Ti-Hf system contain: (Ti,Hf)S titanium and hafnium sulfides, (Ti,Hf)₂SC titanium and hafnium carbo-sulfides, Ti₂O₂S titanium oxysulfides, (Ti,Hf)SCO titanium and hafnium oxycarbo-sulfides, HfO₂ hafnium oxides, Al₂O₃ aluminum oxides

The bulk of nonmetallic inclusions are (Ti,Hf)₂SC carbo-sulfides and (Ti,Hf)S sulfides. All carbides and many oxides are within carbo-sulfides and sulfides. The formation of carbo-sulfides is associated with a monotectic transformation. When the content of sulfur in the alloy is not more than 0.2%, and the carbon content is not more than 0.03%, carbo-sulfides are formed in the alloy solidification range and have an angular-compact shape. If the content of sulfur in the alloy becomes more than 0.2% and carbon content is more than 0.03%, the formation of carbo-sulfides begins in the early stages of alloy solidification. When the content of sulfur and carbon in the alloy is 0.32% and 0.05%, respectively, the formation of carbo-sulfides begins before the α solid solution solidification. In this case, the carbo-sulfide has a dendritic shape and large dimensions. These carbo-sulfides float in a solidifying melt and often reach the surface of the castings. Then, specific surface defects of single-crystal magnets are formed, which are called sulfide spots.

(Ti,Hf)S sulfides are formed in the lower part of the solidification range and have an elongated shape. The formation of these inclusions occurs, probably, by the eutectic transformation. Nitrides of titanium and hafnium were not found in the alloy.

References

- [1] Belyaev, I.V., Bazhenov, V.E., Moiseev, A.V. & Kireev, A.V. (2016). New Fe–Co–Ni–Cu–Al–Ti Alloy for Single Crystal Permanent Magnets. *The physics of metals and metallography*. 117(3), 214-221. <https://doi.org/10.1134/S0031918X16010038>.
- [2] Belyaev, I.V., Moiseev, A.V., Kutepov, A.V., Lomtev, L.A. & Kireev, A.V. (2015). Study of the Effect of Hafnium on the Magnetic Properties of Permanent Magnets with Single-Crystal Structure from Alloy YuNDKT5AA. *Metal Science and Heat Treatment*. 56(11-12), 626-629. <https://doi.org/10.1007/s11041-015-9812-7>.
- [3] Sokolov, V.M., Stomakhin, A.Ja. & Larichkina, R.Ja. (1992). Malootherodnaya tekhnologiya polucheniya otlivok dlya postoyannyh magnitov. *Processylit'ja*. (3), 99-104. (in Russian).
- [4] Pikunov, M.V., Belyaev, I.V., Sidorov, E.V. (2002). *Krystallizatsiya splavov i napravlennoe zatverdevanie otlivok*. Vladimir: Vladimirskiy gosudarstvennyj universitet. (in Russian).
- [5] Grigorovich, K., Burkhanov, G., Shibaev, S., Dolmatov, A., Belyaev, I. & Kolchugina, N. (2009) Fractional gas analysis procedure for determining the contents of oxide and nitride phases in Alnico alloys. *Metallurgija*. 48(3), 187-191.
- [6] Belyaev, I.V., Grigorovich, K.V., Kolchugina, N.B. & Shibaev, S.S. (2010) Effect of the Purity of Starting Materials on the Structure and Properties of Permanent Magnets. *Inorganic Materials*. 46(3), 291-294. DOI: 10.1134/S0020168510030143.
- [7] Sokolov, V.M. (1991). Vliyanie azota na strukturu monokrystallicheskogo splava dlya postoyannyh magnitov. *Izvestija vuzov. Chjornaja metallurgija*. (12), 67-69. (in Russian).
- [8] Malinochka, Ya.N., Kovalchuk, G.Z. (1988). *Sulfidy v stalyah i chugunah*. Moscow: Metallurgiya. (in Russian).
- [9] Bouhemadou, A. & Khenata, R. (2008). Structural, electronic and elastic properties of M₂SC (M = Ti, Zr, Hf) compounds. *Physics Letters A*. 372(42), 6448-6452. <https://doi.org/10.1016/j.physleta.2008.08.066>.
- [10] Wally, P. & Veki, M. (1998). Thermal stability of transition metal carbo-sulfides prepared by combustion synthesis. *Journal of Alloys and Compounds*. 268(1-2), 83-88. [https://doi.org/10.1016/S0925-8388\(97\)00578-1](https://doi.org/10.1016/S0925-8388(97)00578-1).
- [11] Du, Y.L., Sun, Z.M., Hashimoto, H. & Tian, W.B. (2008). First-principles study on electronic structure and elastic properties of Ti₂SC. *Physics Letters A*. 372(31), 5220-5223. <https://doi.org/10.1016/j.physleta.2008.05.079>.