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METAL FILMS ON THE FACE AND IN THE BODY OF DIAMOND CRYSTALS FROM DIAMONDIFEROUS PROVINCES RUSSIAN AND THE WORLD

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Considering the role of the metals in the process of growth and/or dissolution of diamonds, we stick to the most logic and proven mechanism that is used for diamond synthesis in metal-carbon system where metal acts as a catalyst (dissolvent) of carbon and liquid synthesis environment (Alexandrov, 2000). The idea of natural diamonds formation in the mantle in the presence of native metals was for the first time expressed by Wentorf R.H. and Bovenkerk H.P. (Wentorf, Bovenkerk, 1961).

Inclusions in minerals are an important source of information on the physic-chemical properties of minerals formation. At the analysis of diamonds by electronic microscope a number of small inclusions were registered. The presence of native taenite in natural diamonds was originally stated by Bulanova G.P. at al. (1979) and Sobolev N.V. at al. (1981). In later studies (Garanin at al., 1991, Gorshkov at al., 1997, Solodova at al. 2000, Titkov at al., 2006 and others) it was shown, that in the diamonds from different deposits in Yakutia present the inclusions of native metals of micron sizes such as: Fe, Cr, Ni, Cu, Au, Ag, Au-Ag, Ti, Pb, Zn, Fe-Ni, Fe-Cr, Fe-Cr-Ni, Cu-Zn. Most common are the inclusions of native iron and the intermetallic compounds of transitory metals, in which Fe appears to be the main component as well. Less common are native cuprum, titanium, and intermetallic inclusion cuprum, zinc, and other metals, in particular, gold and silver (Titkov at al., 2006).

The traces of interaction of diamond with native metals on natural and manufactured crystals remain on the surface as caverns and the remnants of metal films. The discovering of the fragments of metals with the same compound on the surface and inside the diamond suggest that both the metal films and the inclusions were formed within one evolutionary process of the diamond. The similarity of metal films of natural and synthetic diamonds on the one hand side, and the typomorphism and the characteristic deposit-specific series of films on the other side, testify to the participation of metals in diamond formation process. The nature of metal films and their genetic link to the process of diamond crystallization is a subject of discussion yet. In the given research the focus on the typomorphic classification of metal film fragments of particular deposits. It is for the first time that the typological analysis was made for long fragments of films on the face, polished areas, and fresh crack surfaces of diamonds from the pipes Arkhangelskaya, Snegurochka, International; the data was compared with the data from pipes Lomonosovskaya and XXIII sjezd KPSS (Makeev, Dudar, 2001). Diamonds were cracked with precautions to avoid metal particles intrusion in the samples.

Electro-microprobe analysis of metal films fragments in «Compo» regime revealed the fragments of thin metal films (fig. 1-3) of three types, in the compound of which fifteen elements are presents – metals and their natural combination (Makeev, Kriulina, 2011). Among them five types of elemental compound were discovered for the first time: Ni-Al, Cr-Ti, Fe-Cr-Ni-Mn, Cr-Ni, Ni-Cr-Fe.

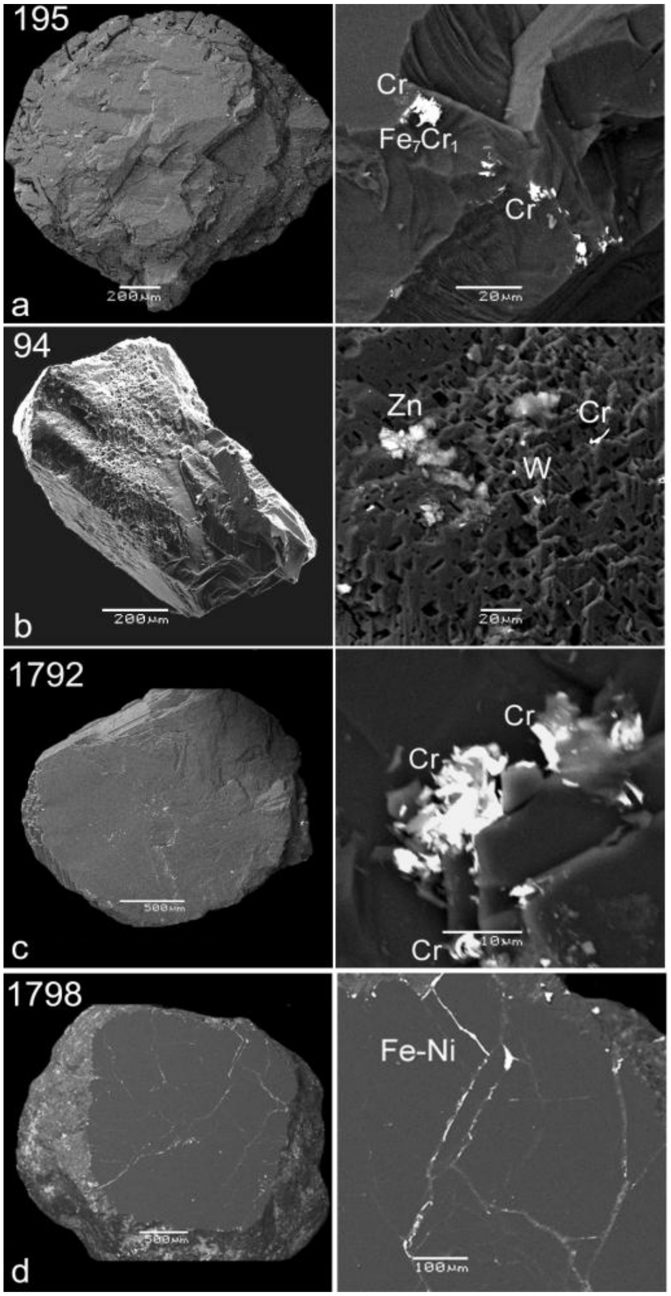

Fig.1. Diamond crystals from Arkhangelskaya pipe with new crack surfaces (a-c) and polishing (d). Left to right: general view magnified surface fragment with metal inclusion, long fragments of metal films.

In energy dispersive spectra (fig. 2) besides metal lines carbon is present, most likely from diamond basis. As metal films are very thin 0.1–1.0 mcm, they are transparent and are not visible under optical microscope even with big magnificence.

The analysis of metal film fragments of the surface and from the inside of diamonds helped to add more typomorphic properties of crystals from pipe of different provinces and deposits of Russia (for example, Lomonosovskaya and International pipes), that referred to one petrochemical type. It has been revealed, that the series of metals (inclusions and film fragments) are typomorphic in particular diamond deposits.

The following thirteen metal film types can be met only in Archangelsk Diamondiferous Province: Al-Cu-Fe, Cu-Zn, Cu-Sn-Pb, Pb, Pb-Sn, Fe-Zn, Fe-Cu, Ni-Cr-Fe, Cr-Fe-Cu-Ni, Ni-Al, Ni-Fe, Cr-Ti, Cr-Ni; only there plumbum and aluminium-based films can be found.For Yakutian Diamond Province the following six metal film types are typomorphous: Cu-Au-Ag, Cu-Zn-Sn-Cr, Zn-Mg, Cr-Zn-Mg, Fe-Ti, W-Ni-Mo, and only there the films with gold, magnesium, tungsten and molybdenum. The wide spread types of metal films that can be found in both provinces in low-titanium kimberlite body types, are the films based on ferrous metal group (Fe, Cr, Ni, Mn), as well as Ag, Cu, Zn, Sn, Ti.

The list of films on 54 crystals from Arkhangelskaya pipe comprises the following fifteen types: pure metals – Cr, Fe, Ni, Pb, and also multi-compound Al-Cu-Fe, Cu-Zn, Ni-Al, Ni-Cr, Ni-Cr-Fe, Fe-Cr-Ni, Fe-Cr, Fe-Ni, Fe-Cr-Ni-Mn, Cr-Ti, Cr-Fe-Cu-Ni. Most common ones contain: metallic chrome – 50% and multi-compound based on iron-chrome-nickel – 40% (table 1). Twenty two diamond crystals were studied from the low-diamondiferous Snegurochka pipe yielding nine metal film types (table 2): pure metals – Fe, Ni, Cr; native brass – Cu-Zn, and Zn-Fe, Cr-Ni, Cr-Ni-Fe, Ni-Cr-Fe, Cu-Zn-Sn-Cr. Most wide-spread are: native brass – 39%; chrome-based compounds

(Cr, Cr-Ni) – 28% and native iron – 17%. On 16 diamond crystals from Lomonosovskaya sixteen types of metal films were detected of the following compound: metals – Ag (Ag_2S), Cu (CuS), Pb (PbS), Zn, Fe, Cr, Ni, Ti and compounds Cu-Zn, Sn-Pb, Sn-Pb-Fe, Fe-Ni, Fe-Cr, Fe-Cu, (Makeev, Dudar, 2001). Most frequent are native iron and ferrous metals-based compounds (~50%), the second half is formed by polymetals. At the analysis of the inner structure of diamonds buried native metal films of 5 to 20 mcm (fig. 1 d) were discovered on the polished surfaces, as well as on

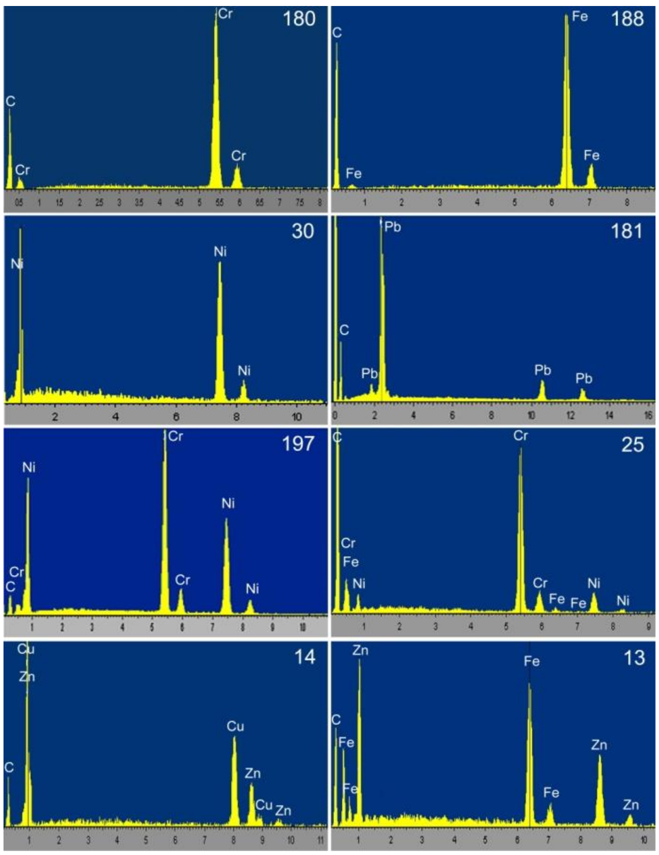

Fig. 2. Energy dispersive spectra of thin metal films on the surface of a diamond from Arkhangelskaya pipe (Ni-Al, Fe-Cr-Ni-Mn, Cr, Fe, Pb, Cr-Ni compounds) and from Snegurochka pipe (Ni, Cu_2Zn – brass, Cr-Fe-Ni and Fe-Zn compounds). In the top right corners of the spectra the number of crystal is shown.

the crush samples of the same crystals from Arkhangelskaya pipe, on the fresh crack surfaces numerous small inclusions were detected; and on the face surface film fragments of the same composition (Fe, Cr, Fe-Ni, Ti-Cr, Fe-Cr) remained (fig.1a-c). Thirty octahedral diamond crystals from International pipe were analyzed. On thirteen crystals there were preserved small fragments (5–30 mcm) of the most stable metal films of eight types: Cr, Ni, Fe, Cr-Ni, Fe-Ti, Fe-Ni, Fe-Cr-Ni-Mn, Zn-Mg (a part of their chemical composition is presented in table 3); among them the most common are Cr – 50%, Cr-Ni – 15%, Ni – 15%. Of the collection of 10 diamond crystals from XXIII sjezd KPSS pipe (Makeev, Dudar, 2001) metal films were found on seven of them. They consist of 13 metals, which form metal films of fifteen types: Fe, Ni, Ti, Zn, Ag(Ag_2S), Cu, Cu-Au-Ag, Cu-Zn, W-Ni(Mo), Fe-Ni, Fe-Cr, Fe-Sn, Cr-Zn-Mg, Zn-Mg, Zn-Mg-Cr. Most common are Zn-Mg-Cr (30%), Fe (21%), Ti (13%), Ni (10%).

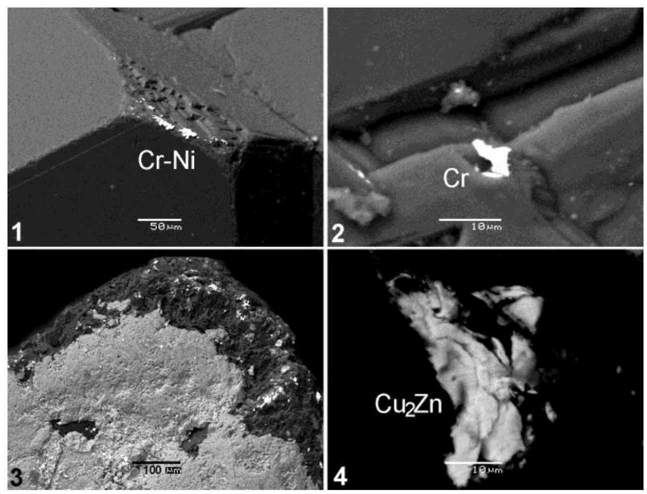

Fig. 3. SEM images of the surface of diamonds from Arkhangelskaya pipe with fragments of films and inclusions of native metals: 1 – diamond N 197 – chrome-nickel compounded film, 2 – diamond N 163 – chrome film; from Snegurochka pipe: 3 – diamond N 25-11 – fragments of chrome-nickel compounded film (bright white spots), under thick (10–20 mcm) dolomite (light-grey) cover, 4 – diamond N 41-01 –natural brass film (Cu_2Zn).

A collection of 25 diamonds of kimberlite field Juina, state Mato Grossu, Brazil (Makeev, Ivanuch, 2004) has a big variety of metal films were discovered: 22 types – Au-Cu-Ag, Ag(Ag_2S), Al-Cu-Fe, Cu(CuS), Cu-Zn-Sn-Cr, Cu-Zn, Zn, Zn-Fe(Mg), Pb(PbS), Sn-Fe, Ti, Fe, Fe-Cr, Fe-Cr-Mo, Fe-Ni-Cu, Fe(Ni,Pt), Fe-Cu, Fe-Sn, Ni, Ni-Fe, Cr-Ni-Fe, Cr-Fe-Cu-Ni, Zr-Yb); a collection of 100 small diamond crystals from Tou-Dou-Gou deposit of Ljaonine province,

Table 1.

Normalized chemical composition (wt.%) of metal films on the diamond crystals from Arhangelskaya pipe

Elements	***163-2***	***163-3***	***165-1***	***182-3***	***182-4***
Al	-	90.22	-	-	-
Cr	100.0	-	100.0	10.98	49.48
Fe	-	2.19	-	6.04	23.24
Ni	-	-	-	82.98	8.48
Cu	-	7.59	-	0.00	18.80
Elements	***183***	***197-2***	***197-3***	***209-2***	***21-1-3***
Al	-	-	-	-	-
Cr	-	48.07	17.10	-	14.94
Fe	95.55	-	-	2.53	76.92
Ni	4.45	51.93	82.90	97.47	8.14
Cu	-	-	-	-	-

Ending table 1

Elements	***204-2***	***215-3***	***217-3***	***219-3***	***221-3***
Al	-	-	2.33	-	-
Cr	17.18	65.27	-	17.60	11.45
Ti	-	34.73	-	-	-
Mn	1.76	-	-	-	-
Fe	67.96	-	-	73.97	88.55
Ni	13.10	-	97.67	8.43	-
Elements	***221-4***	***222-2***	***222-3***	***1795***	***1798***
Al	-	-	-	-	-
Cr	12.15	16.62	15.74	-	-
Ti	-	-	-	-	-
Mn	-	1.46	1.51	-	-
Fe	87.85	72.25	73.87	96.93	89.64
Ni	-	9.67	8.89	3.07	10.36

Note: The analysis of metal films' fragments of the samples 1795 and 1798 were carried out on the polished surface in the body of the crystal.

China – four types of metal films is founded (Fe, Fe-Cr, Ni, Ni-Fe); a collection of 19 diamond crystals form a kimberlite pipe in South-West Angola, Africa (Makeev, Roman'ko, Bryanchaninova N.I., 2009), where were detected four types of metal films (Ag, Al, Fe-Cr, Cu-Zn). As a result of the researches the number of various metal films has grown up and geography of the findings widened significantly. It became clear, that the presence of metal films on diamonds is global, up until now metal films have been found on the diamonds of four continents (Europe, Asia, South America, and Africa). A part of metal films has

Table 2

Normalized chemical composition (wt.%) of metal films on the diamond crystals from Snegurochka pipe

Elements	***14-01-2***	***25-11-2***	***24-01-2***	***24-01-3***
Fe	-	-	-	-
Cr	-	-	-	-
Cu	65.41	79.03	63.57	65.65
Zn	34.59	20.97	36.43	34.35
Sn	-	-	-	-
Elements	***24-19-3***	***24-07-2***	***41-01-2***	***14-02-4***
Fe	-	-	-	6.81
Cr	3.18	100.0	-	-
Cu	73.43	-	65.04	-
Zn	19.53	-	34.96	93.19
Sn	3.86	-	-	-

Ending table 2

Elements	***25-16-2***	***25-11-2***	***25-11-3***	***25-11-4***
Fe	-	4.19	-	-
Ni	-	89.08	17.28	10.14
Cr	100.0	6.72	82.72	89.86
Elements	***25-11-5***	***30-2***	***24-19-2***	***32-01-2***
Fe	2.66	0.98	100.0	100.0
Ni	18.74	99.02	-	-
Cr	78.60	-	-	-

Table 3

Normalized chemical composition (wt.%) of metal films on the diamond crystals from International pipe

Elements	***5906-2***	***5851-1***	***5855-2***	***5823-1***
Cr	100.00	100.00	-	-
Mn	-	-	-	-
Fe	-	-	-	-
Ni	-	-	100.0	100.0
Elements	***5947-1***	***5906-1***	***5855-1***	***5858-1***
Cr	97.27	94.98	53.49	17.77
Mn	-	-	-	1.84
Fe	-	-	-	71.75
Ni	2.73	5.02	46.51	8.64

the same compound as the ones on the diamonds form Middle Timan, Arkhangelsk, and Yakutia; others were discovered for the first time. Now the number of metal film types amounts to 50.

The presence of Zn-Mg, Cr-Zn-Mg, W-Ni(Mo), Zn, Cu-Au-Ag on diamond crystals of highly diamondiferous bodies is a typomorphic characteristic. Mid- and low-diamondiferous bodies are characterized by a bigger variety of chemical compounds of metal films, but also, as a rule, by the absence of precious metals. In kimberlite basement various metal-catalysts and substances interact in fluid phase and influence the kinetics of the oxidizing process up until a full stop (which helps to preserve diamonds) in the presence of precious metals, or contrarily up until full «burning» (dissolution) of a diamond in the presence of active metals (Ni, Fe, Cr, Co, Cu, Pb) in diamondiferous transporter.

Conclusion. The role of metals and their genetic importance for the natural diamond synthesis is not studied enough. It is to estimate the existing paragenesis of diamond with native metals yet; probably it has a connection to: a) fractioning of the mantle basement; b) mobilization of metals in micro-admixture of the diamond itself, and the formation of Me^o emanation as micron inclusions and on the surface of diamonds as native metal fragments; c) metals reduction by gas fluid from the neighboring associate minerals; d) the coexisting formations can be a hardly diagnosable metal-carbon complex. High catalyst activity of native metals in the process of formation of kimberlite bodies together with the longevity of the process most likely influence the real diamondiferous characteristics of those bodies.

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