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# Nanoforms of Secondary Gold in the Tailings Wastes: Placers of Is River, Russia

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**Abstract:** Knowing the mineral composition and relationship between different mineral phases is vary important for planning of mine wastes remediation and possible reuse of tailings material. Study of tailings wastes of gold placer deposits will allow determining the mechanisms of mineral modification and economic potential of extraction of residual gold. Investigations of tailings material of Is River gold placer deposits showed that "new" gold is presented dominantly by nanopatricles and their aggregates. Study of gold grains from tailing piles showed that gold nanoforms modifications are mainly related to amalgamation, chemical alteration of intermetallic components, grains growth due to gold particles adsorption, iron and manganese hydroxides coating and cementation.

**Key words:** Nanogold · Nanoparticles · Placer deposits · Mine wastes · Tailings · Gold modifications

## INTRODUCTION

The main problem of the world's mining activity is a waste disposal, which causes a land loss, pollution of adjacent ecosystems and environmental hazard to neighbourhood population. Knowing of the processes occured in the waste deposits would allow to better assess the level of environmental hazard, suggests the remediation method and/or potential of reuse of the waste material [1].

The disposed mine tailings and waste rock are exposed to atmospheric, hydro- and bio-chemical reagents. Physicochemical interaction with an external environment causes an alteration of the characteristics of primary mineralization of waste materials and its components, forming new stable aggregates and compounds [2-7].

Forming of "new" gold is a wide-spread process in gold mine wastes. This phenomenon was discovered in the wastes of ancient excavations of gold deposits [8]. The same unusual forms of secondary gold were found in the wastes of placers in Mariin Taiga and at the Southern Urals [9, 10]. "New" gold was later described in many placers including Lena Region, Jakutia, Uzbekistan and the Urals [11-16].

Although the small particles have higher total reactive surface area and transport rate, the formation of large gold grains in mine wastes is limited because the tailing deposits are exposed to natural and technogenic (human induced) processes for relatively short time. This is often difficult to distinguish between primary and secondary forms of gold particles, because they experience an influence of almost the same physicochemical processes when they are derived from the source rock and transported to site of deposition.

The "new" gold forms are presented mainly by the nanometric size particles (AuNPs), nano-films and other nanoforms that cannot be observed with conventional investigation methods. Nowadays, an electronic microscopy has been widely used for study of genesis, chemistry, transport and forms of the "invisible" gold natural mineralization [17-19]. Early studies of material obtained form tailings material of different deposits revealed some particularities of secondary gold morphology and grains structure [20]. It was noticed that gold modification mechanism depends on the mineral composition of extracted ore, climate, concentration method, aging, coarsening and total amount of tailigs material. The gold alteration is mainly associated with grain surface processes such as amalgamation, changes

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in intermetallic components composition, grains enlargement due to gold particles adsorption and iron and manganese hydroxides coating and cementation.

However, the nanoforms of "new" gold occurences in the mining wastes have been rarely described in the publications. This study presents the results of nanoscale analysis of samples collected from tailings of the Is River group placer deposits.

## MATERIALS AND METHODS

**Geological and Mining Settings:** The Is river group of platinum-gold placer deposits is related to the Urals Platinum Belt. The placer deposits are situated at about 17 km north-east from Kachkanar vanadium-rich titanium-magnetite ore deposit (Figure 1). Platinum-gold placer deposits were discovered in 1824. Platinum-gold mineralization of this area is associated with Alaskan-Uralian-type Kachkanar Ultramafic complex composed dominantly of gabbro-clinopyroxenite [21]. Primarily, platinum was a target of extraction as the most economically important element. Later, gold extraction started after platinum resources were exhausted.

The ultramafic rocks are characterized by very low gold grade. However, zones of hydrothermally-altered rock with higher gold grade have been locally discovered. The veins material within these zones, presented mostly of plagioclase and amphibole with occurences of pyrite and chalkopyrite, might be considered as the main source of placer gold of Is River [22].

Hydraulic mining and dredging methods have been used for gold extraction at this area. For long period of exploitation, placer deposits of Is River have been reworked in many places one or more times that contributed to intensive alteration of the waste material.

**Sampling and Laboratory Study:** Samples were collected along the Is River stream channel from tailings piles of different age. The samples material was concentrated in the field with panning and spiral sluicing separator [23]. Later, in laboratory, the treatment with heavy liquid and magnetic/electromagnetic separation were used for further concentration. To get the separate gold grains available for nanoscale analysis the concentrated material was sorted out with an optical microscope.

Surface of the gold grains was investigated at the Department of Mineralogy and Petrography of Perm State University using the cold cathode analytical JEOL field emission scanning electron microscope (SEM) JSM 7500F

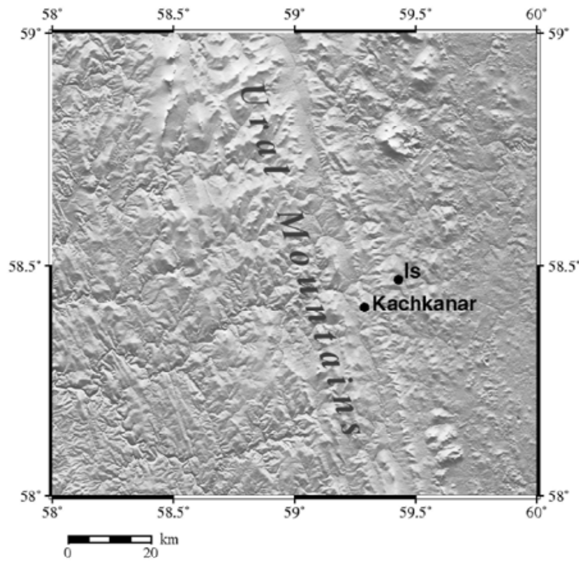

Fig. 1: Location map of the study area.

with magnification up to 1,000,000. Elemental and chemical composition of gold particles was determined using JEOL JSM 6390LV scanning electron microscope with the Energy Dispersive Microanalysis (EDS) and the Wavelength Dispersive Microanalysis (WDS) microprobe modules of Oxford Instruments.

## RESULT AND DISCUSSION

The obtained micrographs of gold nanoparticles demonstrate the variety of forms of gold occurences in the mine tailings environment. The previous observations showed that characteristic forms of gold encountered in the mine wastes from different placer deposits are presented by well and moderate rounded flattened grains, cloddy porous aggregates and "mustard" gold. Also there are noticed the varying grained, lamellar aggregates, fine-grained euhedral assemblages, dendrite/skeletal aggregates, etc. [24-27].

Primary phases of AuAg system were most frequently observed in the central part of investigated grains, sometimes as small relicts. The fineness of primary gold ranges from 600 to 990 with predominant variations from 850 to 900. Beyond the primary AuAg phases, microprobe analysis revealed a presence of phases of AuCu system (close to $Au_3Cu$), which form the lamellar accretion with AuAg phases probably in result of decomposition of AuAgCu alloy. Small amount of the intermetallic compounds of AuPb phase system analogous to hunchunite ($Au_2Pb$) were rarely observed.

Table 1: Chemical composition of analyzed gold grains (wt. %).

| Grain No | Analized portion of grain | Au | Ag | Hg | Cu | Pb | Σ |
|---|---|---|---|---|---|---|---|
| 1 | $Au_2Pb$ phase | 58,6 | 0,88 | 4,53 | 0,04 | 32,9 | 96,95 |
| 1 | $Au_2Pb$ phase | 57,91 | 0,97 | 4,55 | 0,03 | 33,41 | 96,87 |
| 1 | Au-Ag phase | 79,50 | 11,97 | 5,45 | 0,75 | 0,01 | 97,68 |
| 1 | grain core | 96,22 | 3,54 | 0,04 | 0,02 | 0,00 | 99,83 |
| 1 | grain rim | 80,61 | 4,59 | 11,65 | 0,19 | 0,10 | 97,14 |
| 2 | AuAg grains of different fineness | 77,90 | 18,44 | 0,15 | 0,00 | 0,00 | 96,49 |
| 2 | | 91,18 | 5.79 | 0.08 | 0.05 | 0.00 | 97.10 |
| 2 | | 81,93 | 16,64 | 0,10 | 0,06 | 0.00 | 98,73 |
| 2 | electrum | 59,58 | 33,27 | 1,04 | 0,00 | 0,00 | 93,89 |
| 2 | rind | 72,97 | 6,15 | 15,24 | 0,00 | 0,00 | 94,36 |
| 3 | balky grains | 96,90 | 0,29 | 0,60 | 0,00 | 0,21 | 98,01 |
| 4 | grained aggregate | 82,97 | 0,91 | 12,86 | 0,07 | 0,00 | 96,81 |
| 5 | grains in balky Àu | 77,93 | 13,15 | 5,90 | 0,97 | 0,00 | 97,95 |
| 6 | Assemblage with Pt grain | 80,26 | 12,2 | 4,78 | 1,09 | 0,07 | 98,40 |
| 7 | Spherical grain | 66,84 | 1,52 | 26,70 | 0,16 | 0,00 | 95,22 |
| 7 | Au amalgams | 63,33 | 0,52 | 29,32 | 0,00 | 0,00 | 93,17 |
| 8 | ÀèAg grain | 92,18 | 4,43 | 0,75 | 1,07 | 0,01 | 98,44 |
| 8 | Amalgam rim | 65,15 | 0,80 | 28,72 | 0,06 | 0,00 | 94,73 |
| 9 | Dark «olive» Àu | 91,54 | 0,49 | 5,55 | 0,00 | 0,03 | 92,61 |
| 9 | Light-colored phase | 95,80 | 0,46 | 4,75 | 0,01 | 0,00 | 96,74 |
| 10 | Core of ÀuAg grain | 83,09 | 14,62 | 0,03 | 0,00 | 0,00 | 97,74 |
| 10 | Grained rim | 78,55 | 4,10 | 13,58 | 0,11 | 0,08 | 96,42 |
| 11 | CuÀu grain | 86,58 | 0,61 | 0,14 | 10,44 | 0,00 | 97,77 |
| 11 | AuAg lamellae | 85,96 | 5,14 | 3,47 | 2,24 | 0,03 | 96,84 |
| 12 | AuCu phase | 94,81 | 0,22 | 0,88 | 1,10 | 0,00 | 97,01 |
| 12 | Fine fraction | 70,67 | 0,48 | 8,15 | 19,94 | 0,00 | 99,24 |
| 13 | Internal AuCu rim | 71,7 | 0,50 | 4,11 | 24,93 | 0,06 | 101,3 |
| 13 | Outer AuCu rim | 87,76 | 0,28 | 4,64 | 0,36 | 0,28 | 93,22 |
| 14 | Primary grain core | 95,16 | 2,86 | 0,21 | 0,10 | 0,00 | 98,33 |
| 14 | Rim phase | 88,18 | 0,10 | 8,60 | 0,12 | 0,02 | 97,02 |
| 14 | Rim phase | 87,60 | 0,18 | 8,95 | 0,08 | 0,06 | 96,87 |
| 15 | Light-colored phase | 68,75 | 6,01 | 21,85 | 0,37 | 0,00 | 96,98 |
| 15 | Brown phase | 89,91 | 0,71 | 3,97 | 0,09 | 0,18 | 94,86 |
| 16 | Core relict | 99,46 | 0,55 | 0,41 | 0,00 | 0,05 | 100,47 |
| 16 | Light-colored phase | 79,86 | 0,47 | 15,68 | 0,04 | 0,00 | 96,05 |
| 16 | Brown-colored phase in rim | 92,65 | 0,17 | 2,90 | 0,00 | 0,33 | 96,05 |
| 17 | Inclusion in $Cu_2Zn$ | 48,87 | 10,7 | 43,97 | 2,58 | 0,88 | 97,37 |
| 18 | Delicate assemblage | 68,30 | 1,30 | 0,00 | 15,22 | 12,35 | 97,17 |
| 18 | Delicate assemblage | 65,85 | 1,39 | 0,07 | 17,88 | 13,73 | 98,92 |

Inclusions of gold amalgam were encountered in CuZn grains, but secondary character of these grains was not evident. The studied grains also contain the intermetallic compounds of Pt-Fe group elements. The result of microprobe analysis of chemical composition of gold grains is presented in Table 1.

Previous studies established that the process of chemical and bacterial oxidation is a main mechanism of gold release from primary phases. The other mechanism playing significant role in gold modification is an amalgamation, which can be caused by the mercury from both the technogenic and natural sources. Because of low rate of mechanical processes in the tailings, the transformation and enrichment of gold is governed mainly by reactions of auriferous solutions and waste material.

The solubility of gold increases when size of particles decreases. Therefore, gold leached from primary system migrates mostly in form of colloidal nanoparticles. The following adsorption and self-assembling processes lead to formation of different assemblages of divided AuNPs or fine aggregates such as "mustard" gold. Some micrographs of the forms of gold nanoparticles and nanoparticles grouping observed in the material of tailing wastes of Is River placers are presented in Figure 2.

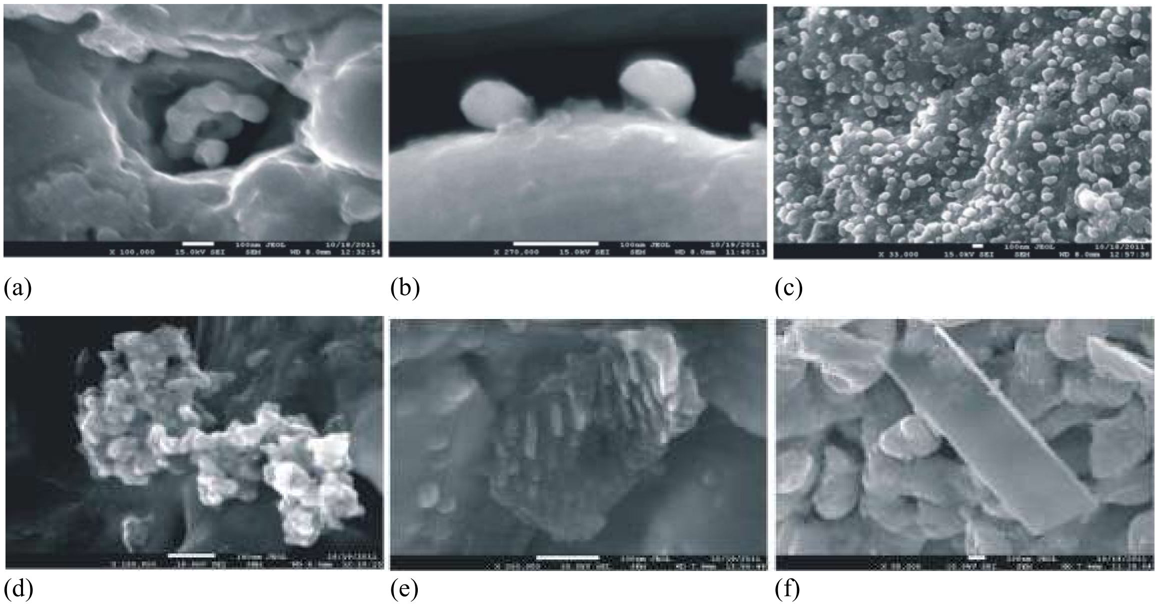


Fig. 2: Micrographs of nanoforms of "new" gold from tailings of Is River placer deposits: a) gold nanoparticles filling the etch pit, b) single colloidal gold particles adsorbed onto the microcrack wall, c) single gold particles and aggregates on the grain surface, d) aggregate built-up by gold nanoparticles, e) stalactite-shape aggregate, f) gold nanofilm aggregate on the grain surface.

## CONCLUSION

On the basis of the analysis of results of this study and preliminary observations it was confirmed that gold modification in the mine waste tailings is governed predominantly by the natural processes, which are characteristic for placer gold genesis, with minor influence of the technogenic factors applied during concentration operation. The results of this study will be used in further research aimed to design the effective methods of gold extraction from tailing wastes.

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