

The Effect of the Nickel Sulphide Alloys Structure on Their Electrochemical Oxidation Parameters

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Abstract: The granulation of nickel sulphide alloys results in formation of the ultrafine structure because of their reactivity is increased in the hydrometallurgical processing. The phase composition and phase size of nickel sulphide alloys granulated was studied by X-ray and optical microscopy methods. It is shown the high cooling rate leads to the crystallization of non-equilibrium phase and dispersion of a metal component. The parameters of the electrochemical oxidation of nickel sulfide granular alloys in sulfuric acid solution were estimated. The initial potentials of phase components oxidation of nickel sulfide alloys granulated were defined. The rate of electrochemical oxidation of nickel sulfide alloys granulated is higher than that at slow-rate cooling.

Keywords: nickel sulphide, nickel convertor matte, sulfur, microstructure, electro oxidation, passivation.

1. INTRODUCTION

Electrolysis is one of processing convertor matte methods. The process is characterized by sulphur conversion in elementary state [Chizhikov D.M et al. (1977), Chizhikov D.M. et al. (1962), Selivanov E.N. et al. (2010)]. On the one hand the significance of this way for processing technology of copper-nickel sulphide material has been justified the realization excludes casting process of sulphide-metal anodes, on the other hand into the atmosphere emissions of sulphur dioxide is eliminated. Therefore the work out of electrochemical oxidation scientific bases of an no equilibrium sulphide nickel alloys crystallized [Nechvoglod O.V. et al. (2012), Nechvoglod O.V. et al. (2012), Zalazinskii M.G. et al. (1984)] is actual. It is assumed under no equilibrium conditions the alloys cooling results in the formation of phases having properties differencing from the stoichiometric sulphides and pure metals.

The article purpose is to study the structure of a copper - nickel metal - sulphide alloys cooled no equilibrium and estimation of its impact on the electrochemical oxidation processes. To achieve the above purpose the tasks were taken into account such as: the estimation of the cooling rate effect of sulphide nickel alloys on the structural parameters of the phases formed, the study of the process features in the electrochemical oxidation of sulphide nickel alloys granulated, the estimation of the electrochemical oxidation parameters of sulphide nickel alloys

2. METHODS

To study the cooling rate effect on the structure of nickel sulfide alloys and subsequent electrochemical oxidation the samples containing (in percent) were taken:

	Ni	Cu	Fe	Co	S
Sample 1	72,1	-	-	-	27,5
Sample 2	74,3	3,2	0,1	0,3	16,8

Sample 1 was synthesized by melting of PNE 1s nickel powder together with elemental sulphur by means of heating slowly the mixture up to 1250°C in a graphite crucible in the electric resistance furnace. Sample 2 was presented an industrial convertor matte of Ltd. "Ufaleynickel".

To obtain the samples with a structure closed to the equilibrium a method of melt extraction in quartz tubes is used. This technique is compared with slow cooling relatively. The cooling rate is calculated as the ratio of the melt temperature difference (t_m) and the crystallization start temperature (t_c) for the existence samples duration in the molten state. When cooling of the melt in a quartz tube (internal diameter of the tube is 4.5 mm, wall thickness is 1 mm) the cooling rate was ~ 10 deg/s.

In a laboratory setting the high cooling rates were achieved by means of their melt granulation in water [Udoyeva L.J. et al. (2008)]. Duration (τ , s) of the melt drops cooling to the temperature of crystallization in full is evaluated by the equation (1).

$$\tau = \frac{d \cdot (C_p \cdot \rho)}{6 \cdot \alpha \cdot \ln[(t_m - t_v) \div (t_c - t_v)]}, \quad (1)$$

where: d is drop size, m ; C_p is heat capacity melt being $0,7 \text{ kJ/kg } ^\circ\text{C}$ at $1200 - 1300 \text{ } ^\circ\text{C}$; ρ is converter matte melt density being $5,74 \cdot 10^3 \text{ kg/m}^3$; α is heat transfer coefficient in melt – gas system being $10^3 \text{ W/m}^2 \text{ } ^\circ\text{C}$; t_m , t_c , t_v are melt, its crystallization and vapour temperatures being 1250 , 950 and $100 \text{ } ^\circ\text{C}$, respectively. Using expression (1) the duration of granule cooling is calculated by substitution of controlled and tabular value. The cooling rate of samples is found as the difference ratio of temperatures ($t_m - t_c$) for cooling duration (τ). The average diameter of samples granulated is $1,4 \text{ mm}$. The cooling duration value of granules is $0,15 \text{ s}$, cooling rate being about 1000 deg/s .

The phase composition of the samples is estimated in an automated XRD 7000C Shimadzu diffractometer. Decrypting data is carried out on a Powder Diffraction Files database. The microstructure was studied by optical microscope Olympus GX-51. The electrochemical oxidation of sulphide alloys is conducted in setting including the measurement cell combined with IPC potentiostat. Processing of data is performed by IPC-2000 software system. To identify features of the sulphide-metallic alloys electrochemical oxidation the methods of voltampermetry with linear potential sweep are used. It allows to obtain data on the oxidation potentials of the samples phase components. Using the value the oxidation mechanism of copper nickel sulphides and complex sulphide-metal alloys is explained. Polarization curves of the samples anodic oxidation are read in 1 M sulphuric acid, the sweep rate of the potential being 10 mV/s in the $300 \div 2000 \text{ mV}$. For electrochemical studies the samples granulated and cooled slowly were placed in a cage after it is filled by epoxy resin. Electrical contact is provided by copper wire. Resin having been hardened, front surface of samples is polished. Sample of metallic nickel is presented cylinder cross-sectional area is $15,2 \text{ mm}^2$. The surface area of 1 and 2 samples slowly cooled is $15,2 \text{ mm}^2$ and those granulated do $15,4$ and $9,4 \text{ mm}^2$, respectively.

3. RESULTS

3.1 The Influence of Cooling Rate of Sulphide Samples on Their Microstructures

According to X-ray diffraction XRD (Fig. 2) in the sample 1 synthesized heazlewoodite (Ni_3S_2), godlevskite (Ni_7S_6), millerite (NiS) as well as the phase of metallic nickel having been crystallized by slow cooling of the alloy are identified. According to metallographic analysis (Fig. 3) in the plane of the micro photo the particles of metallic nickel have a size of $2-3 \text{ mm}$ and are within the nickel sulphide, as well as on the pore borders.

The main phase component of sample 1 granulated is $\text{Ni}_{3+x}\text{S}_2$. Metallic nickel phase is not detected. It speaks about the rapid cooling results in a stabilization of non-equilibrium sulphide phases with metals dissolved in these.

Sample 2 cooled slowly is formed by nickel sulphide phase and fragment form particles consisting of a solid solution based on nickel. Metallic nickel in the form of emulsion point field is found in the nickel sulphide phase and separate large crystals. The particle size of nickel reaches $100-400 \text{ nm}$. On micro photo areas corresponding to the allocation of nickel

sulphide and $\text{Ni} - \text{Ni}_3\text{S}_2$ eutectic are pointed out. Pattern 2 granulated is formed phases of Ni_3S_2 and metallic nickel. On the micro photo of the sample 2 granulated micro section compared to the that cooling slow large particles of metallic nickel are not detected.

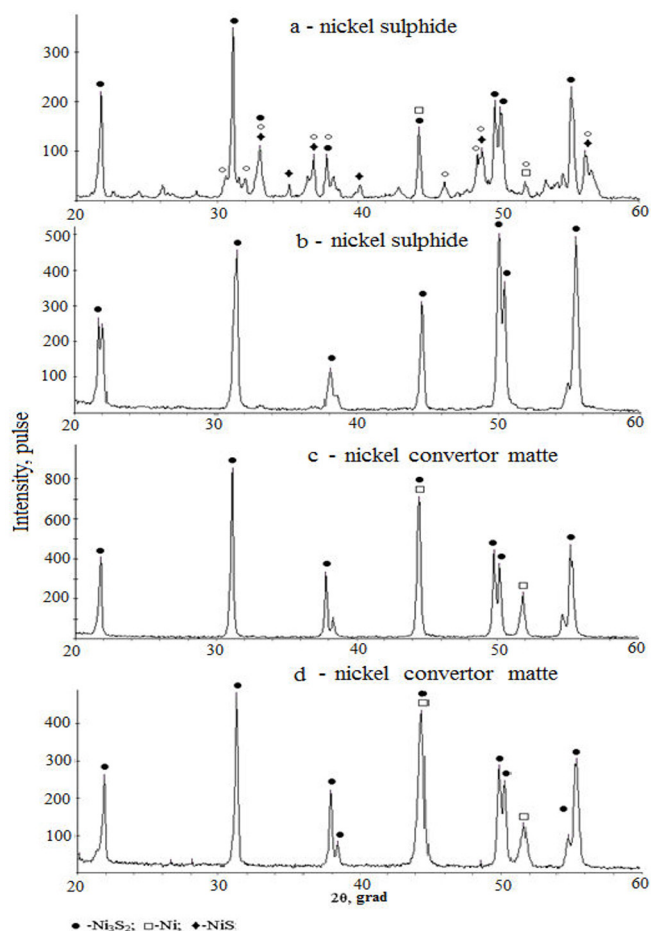


Fig. 1. X-ray diffraction of nickel sulphide samples having been cooled at 10 (a, c) and 1000 (b, d) deg/s rates

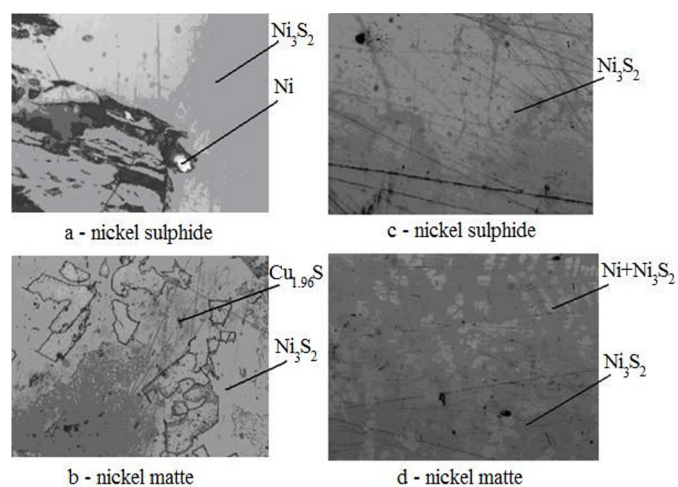


Fig. 2. The microstructures of samples 1 and 2 having been cooled at 10 (a, b) and 1000 (c, d) deg/s rates

3.2 The Influence of Sulphide Samples Microstructures on Parameters of Their Electrochemical Oxidation

It is shown earlier [Nechvoglod O.V. et al. (2012)] the electrochemical oxidation rate of nickel sulphide granulated is higher than that slowly cooled: ($8,8 \cdot 10^{-8}$ and $1,3 \cdot 10^{-7}$ g/s, respectively). For detailed study of the oxidation mechanism of the sulphide nickel alloys cooled by different rates voltampermetric characteristics of the samples were obtained. At the potential of electrodes in 0.770 V (Table 1) the electrochemical oxidation of sample 1 slowly cooled (Fig. 3) is started and reaches a maximum about 1.290 V. During anodic oxidation of Ni_3S_2 to NiS and elemental sulphur forming a layer of insoluble products on the electrode surface are likely to form [Price D.C. et al. (1982), Ghali E. et al. (1980)]. A maximum rate of oxidation having been reached, nickel sulphide is passivated by product soluble hardly film of electro oxidation. Decrease in the rate of anodic processes is due to the conditions under which the oxidation of sulphide (Ni_3S_2) is limited by the counter diffusion of Ni^{2+} and SO_4^{2-} ions across solid oxidation products. The fractures in the curve can be explained as an intermediate NiS and elemental sulphur. In addition to considerable polarization (electrode potential is above 1.4 V) is possible oxidation of sulphide sulphur in thiosulphate. Thus oxidation of nickel sulphide proceeds in the sequence: $\text{Ni}_3\text{S}_2 \rightarrow \text{NiS} \rightarrow \text{Ni}^{2+} + \text{S}$.

Table 1. The potentials (ϕ) and currents (i) of the oxidation of samples having been cooled at different rates (b - the beginning, e- extreme)

	Nickel		Nickel converter matte			
	ϕ_b/ϕ_e , mV	i_b/i_e , A/m ²	ϕ_b/ϕ_e , mV	i_b/i_e , A/m ²	ϕ_b/ϕ_e , mV	i_b/i_e , A/m ²
Cooling rate is 10 deg/s						
1			770/1290	25/3715	-/1465	-/3315
2	95/370	308/2100	78/1180	130/3900	-/1300	-/4000
Cooling rate is 10^3 deg/s						
1			910/1310	15/620	-/1480	-/3410
2	-	-	860/1130	85/2070	-/1360	-/3780

The electrochemical oxidation of nickel converter matte granulated is begun at the potential of the anode in 0.790 V. Limit values of the current densities in 1280 and 2090 A/m² are achieved at potentials 1.04 and 1.22 V, respectively. In the state of passivity at v being 10 mV / s through the anode the current flows. Its density is 1460 A/m². The density of the current flowing through the electrode during passivation is 3200 A/m². Nickel converter matte granulation does not influence by practically the start and peak potentials of oxidation but increases the rate of the anode dissolution in passivation film.

Data presented on the electrochemical oxidation of sulphide nickel alloys cooled at different rates can be used for work out of new environmental ways of nickel converter matte processing.

Anodic oxidation of sample 1 granulated runs incrementally. This trend is marked for sample cooled slowly. The curve fractures related to the metal phase oxidation of nickel have

not been found. Sulphide phase oxidation of sample 1 granulated is started at a potential about 0.910 V and the maximum current density has been achieved 3620 and 3410 A/m² at electrode potentials in 1.31 and 1.48 V.

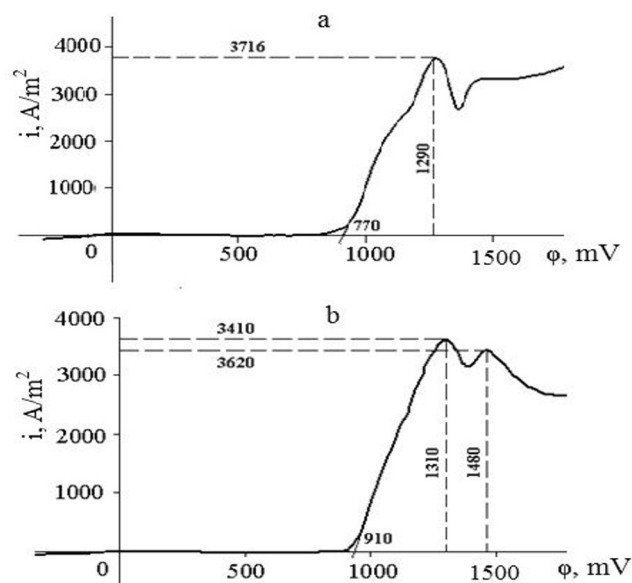


Fig. 3. The voltampermetric curves of the electrochemical oxidation of nickel sulphide (sample 1): a is nickel sulphide cooled slowly; b is nickel sulphide granulated

According to experiments having been carried out (Fig. 4) on the electrochemical oxidation of sample 2 the presence of the metallic phase in the alloy affects the characteristic potentials of its oxidation. The phase metalized oxidation of sample 2 cooled slowly is begun about 0.075 V and the maximum rate of oxidation is achieved at 0.360 V. Sulphide phases begin to be oxidized from 0.750 V and have a maximum oxidation rate at 1.10 V and 1.21 V.

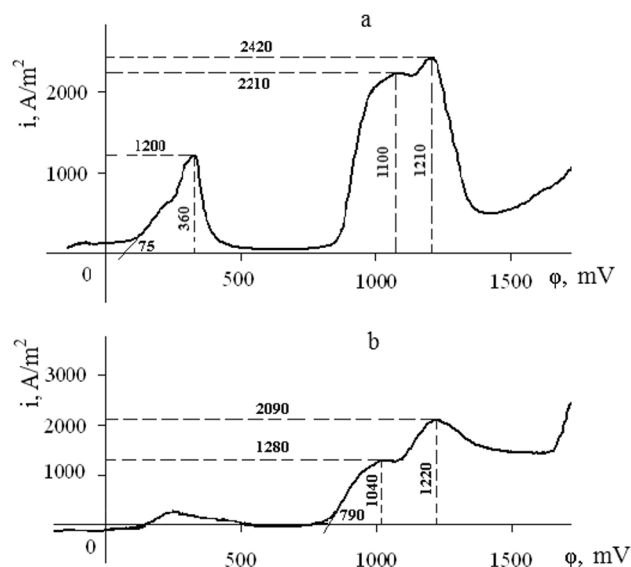


Fig. 4. The voltampermetric curves of the electrochemical oxidation of converter matte: a is converter matte cooled slowly; b is converter matte granulated

3. CONCLUSION

The cooling rate influence of sulphide-metal melts on the composition of phases formed is defined. It is shown the main phase components nickel sulphide cooled slowly are heazlewoodite (Ni_3S_2) and nickel metal. Nickel sulphide granulation results in a stabilization of the $\text{Ni}_{3+x}\text{S}_2$ no equilibrium phase and the decline of the metal phase fraction up to its complete disappearance. During slow cooling of sulphide nickel alloys metalized (nickel convertor matte) the particle size of metallic nickel is 100-400 nm. Granulation leads to dispersion of metallic nickel (particle size is reduced to 10 nm) in the $\text{Ni}_{3+x}\text{S}_2$ phase bulk.

Electrochemical oxidation of the samples proceeds incrementally and corresponds to transitions: $\text{Ni}_3\text{S}_2 \rightarrow \text{NiS} \rightarrow \text{Ni}^{2+} + \text{S}$. The oxidation of nickel convertor matte phase components depends on the initial oxidation of metallic nickel. Oxidation potentials of the sulphide nickel alloys phase components are determined

The differences detected during the electrochemical oxidation of nickel sulphide alloys obtained at different cooling rates are due to the structure of samples and forms of existence metals. On the surface of the sample granulated the oxidation of sulphide sulphur to intermediate products of reaction takes mainly place. On the surface of the sample cooled slowly convertor matte along with the oxidation of sulphide leaching of metallic phase sites proceeds.

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REFERENCES

- Chizhikov D.M. et al. (1962). Hydrometallurgy of sulphide alloys and mattes, 207p. The Academy of Sciences of the USSR, Moscow.
- Chizhikov D.M et al. (1977) Electrometallurgy of copper-nickel sulfide alloy in aqueous solutions, 264 p. Nauka, Moscow.
- Ghali E., Maruejouis A, Deroo D. (1980). Electrodisolution de la heazlewoodite en milieu chlorhydrique. Journal of Applied Electrochemistry. Vol. 10. P.709–719.
- Nechvoglod O.V., E.N. Selivanov, S.V. Mamyachenkov. (2012). The electrolysis of granulated copper-nickel matte, PP 601-620. Fray International Symposium. Metals and materials Processing in Clean Environmen. Aqueous. Low Temperatures and Electrochemical Processing. Vol.6
- Nechvoglod O.V., Selivanov E.N., Mamyachenkov S.V. (2012). Effect of Structure on the Electrochemical Oxidation Rate of Copper and Nickel Sulfides, PP 383-387. Defect and Diffusion Forum. Vol. 326-328.
- Price D.C., Davenport W.G. (1982) Anodic reactions of Ni_3S_2 , β - NiS and nickel matte, P. 281–290. Journal of Applied Electrochemistry. Vol. 12.
- Selivanov E.N. et al. (2010) The electrochemical oxidation of nickel sulfide-metal alloy, PP. 20-25. University News. Non-ferrous metallurgy. Vol. 2.
- Udoyeva L.J. et al. (2008). The structure of the granulated copper- nickel convertor matte, PP.41-43. Non-ferrous metals. Vol. 10.
- Zalazinskii M.G., Khudyakov I.F. (1984) Oxidation of low-nickel sulphide in sulphuric acid solutions, PP. 2118-2120. Journal of Applied Chemistry, Vol. 9.