

THE EFFECT OF COPPER CONTENT IN THE MATTE ON THE DISTRIBUTION COEFFICIENTS BETWEEN THE SLAG AND THE MATTE FOR CERTAIN ELEMENTS IN THE SULPHIDE COPPER CONCENTRATE SMELTING PROCESS

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Abstract

This paper presents the results of investigating the dependence of distribution coefficient $L^{S/M}Me$ for: Cu, Zn, Pb, Sb, As, Ni, Ag, Au and Bi, between the slag and the matte, on the copper content in matte. The research was conducted under industrial conditions of copper concentrate smelting, in the reverberatory furnace in the copper smelter in Bor, Serbia. It was found that with the increase of the copper content in the matte, distribution coefficient between slag and matte for Cu, Zn and Pb increases, for Ag and Se decreases, while for Ni, As and Sb has an insignificant change. Au and Bi are almost entirely concentrated in the matte.

Key words: copper concentrates, smelting, $L^{S/M}Me$, matte, slag.

1. Introduction

In the pyrometallurgical process of copper production the phase of sulphide concentrate melting is always present, during which the greatest amount of material from the batch is

removed as the slag, while the copper is concentrated in the sulphidic binary system - matte ($Cu_2S - FeS$) [1, 2]. Distribution of copper between two phases, slag and matte, depends on many parameters such as composition of the slag [3-8], matte

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composition [9] as well as on technological parameters of the process [4]. Distribution of other elements contained in the concentrate was not studied separately, although in addition to the theoretical significance, there are practical implications from the aspect of utilization of the components in the concentrate and from the aspect of emission of harmful components in the environment [10, 11].

Besides the copper, other non-ferrous metals are present in the concentrates (Ni, As, Co, Bi, Pb, Zn, Se, Te ...) as well as precious and platinum metals (Au, Ag, Pt, Rd ...). In the melting stage, during which useless oxide phase in the form of slag is separated from the matte, distribution of these elements between the slag and the useful phase - matte is important. However in the next stages of slag processing usually only the copper is utilized, while other components are permanently lost. Also, together with the flue gases, in the form of dust, a certain amount of non-ferrous metals and sulfur in the form of SO₂ gas are distributed in the environment [12]. Transfer of non-ferrous and precious metals during the melting process into the matte phase, is an important segment in the overall economy of the pyrometallurgical treatment in the copper production. Some authors have developed mathematical models which describe dependence of the contents of certain components in the slag on the input parameters of the process [13, 14, 15].

In this paper the results of research on the influence of copper content in the matte on the other metals coefficient of distribution between slag and matte is presented. Results are obtained in a specially organized

experiment, under industrial smelting conditions in the reverberatory furnace, in the copper smelting complex in Bor (Serbia). The objective of this research was to determine the influence of the copper content in the matte on the coefficient of distribution between the slag and the matte, for the most frequently present metals, during the melting phase, with an aim to enable the control of the utilization of individual components.

2. Experimental

The experiment, whose results are presented in this paper, was carried out under industrial conditions of the copper concentrate smelting process in the reverberatory furnace in Bor, according to the described procedure [7]. In this experiment, samples of slag and matte were gathered in order to determine the contents of Cu, Au, Ag, Pb, Zn, Ni, As, Sb, Se and Bi with the aim to determine their distribution coefficients between these phases. Matte quality, determined by the contents of copper in the matte, ranged from 36.31% Cu to 42.12% Cu, in the investigated system. Technological parameters on the day the experiment was conducted were stable, indicating that the obtained results are correct.

For a quantitative determination of the elements with concentration above 0,1%, an optical emission spectrograph OES JARRELL-Ach 70.000 (USA) was used, while for the elements with a concentration below 0.1%, a mass spectrograph JOEL JMS 0.1MB (Japan) with the ionic optical system Matauh.Herzog was used.

3. Discussion of results

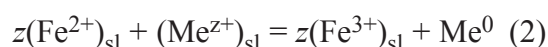
The distribution of an element between the slag and the matte phase, and the conditions which lead to maximum recovery of an element into the copper matte or its complete elimination into the slag, are very important for metallurgists. The distribution coefficient for copper and other elements, between the slag and the matte, is defined as follows:

$$L_{Me}^{S/M} = \frac{(Me)}{[Me]} \quad (1)$$

where: (Me) - the metal content in the slag, [Me] – the metal content in the matte.

The distribution of the elements between the slag and the matte depends on the chemical reactions in the slag, the chemical reactions on the slag - matte boundary layer, as well as on sedimentation of metal through a layer of slag [4].

Jelkanen et.al. [16] suggest that the reduction of oxides of more noble metals (relative to iron), dissolved in slag, takes place through a rapid disproportionation reaction of the following type:



That leads to the formation of the fine metallic dispersion in the slag with a very low settling rate. Magnetite, settling through the slag layer, encounters a phase boundary layers, slag - matte, where it reacts with the iron sulfide from the matte while discharging SO₂ gas. The SO₂ gas, created this way, on its way through the slag layer towards the furnace atmosphere, creates a “flotation” effect, which pulls suspended sulfide particles in the slag towards the surface of

the melt retaining them in the slag until its final discharge from the furnace. On its way to the top, the bubble brakes or merges with other bubbles, this way loses its matte carrying membrane effect, which results with the occurrence of matte droplets in the slag. Those matte droplets, this way, are not the consequence of the primary *smelting* of concentrates. Such obtained copper loss in the slag is usually defined as mechanical loss [17]. However, besides the copper, in this matte droplets other non-ferrous, rare and precious metals are dissolved, having the same ratio as in the matte, which results with a portion of trace metals which is mechanically retained in the slag layer. Fig.1. shows the matte droplet within the bubble in the slag, during the “flotation” through a layer of slag.

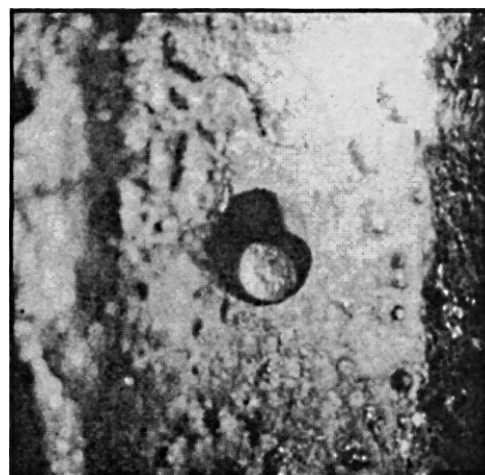
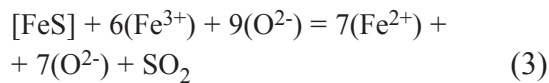


Fig. 1. Microphotography of the hardened slag, obtained from the process of sulfide concentrate smelting.

In addition to the mechanically retained elements in the smelting slag, due to the lack of time required for the complete division of layers, the slag contains chemically retained

elements as well, such as: copper and other non-ferrous, rare and precious metals. Slag melt contains oxygen in three forms, namely: as free O^{2-} anion, connected with a single valence to the silicate complex O^- and joined with both valences with the silicate complex O^0 . Since the slag melt is in contact with the gas atmosphere containing oxygen, and that the magnetite is formed during the process of concentrate smelting, as well as the input of magnetite with the converter slag (in some smelters), the activity of O^{2-} ions in the slag is higher than the one corresponding to the equilibrium state of the system $FeO - SiO_2 - CaO - Al_2O_3 - Fe_3O_4$. The fact that there is an "excess" of O^{2-} in the slag, leads to the reaction taking place in the slag layer or in the slag- matte phase boundary:



Reaction (3) leads to promoted reduction of the Fe^{3+} ion, which adds to the further progress of disproportionation reaction (2) with the precipitation of fine dispersion of metallic copper. In order to maintain electrical neutrality of the system, one "excess" O^{2-} ion oxidizes two ferrous ions to ferric ions, so that the activities of Fe^{3+} and "excess" O^{2-} ions are proportional for the given slag composition.

In earlier studies all impurities in the fayalite slag were presented only in the oxide form [18] which is true only for Cu, Co, Ni, Pb, Sn and Zn. Nagamori and Mackey [19] showed that in addition to the oxide solubility in the slag there is a sulfide solubility as well, when dissolved sulfur in the slag attracts an element, with which it

builds a stable sulfide, into the slag phase. Mono-atomic solubility was also registered, which occurs when the oxides and sulfides of elements are unstable under the smelting conditions, so the element dissolves in the metal or gaseous form (Ag, As, Au, Bi, Sb, Se, Te). Molecular solubility occurs when an element is forming compounds with iron, which are very stable under the conditions of the smelting process (S, Se, Te). Furthermore, there is also a halogen solubility, when an element forms a very stable halides (Ag, Au, Cu, Pt) under the smelting conditions. In this study chlorine content was determined in the slag within the limits of 0.01 - 0.03% Cl and in the matte within 0.01 - 0.02% Cl. These facts indicate that all mechanisms for the solubility of elements in the slag and the matte are present, and that the distribution coefficient $L_{Me}^{S/M}$ depends on the affinity ratio of individual elements present in the slag - matte system according to: Fe^{2+} , Fe^{3+} and O^{2-} .

Oxide, sulphide and mono-atomic mechanisms of solubility of elements in the slag can be confirmed by analyzing the diagrams of sulfur and oxygen partial pressure at 1200 °C which shows the stability of metals, oxides and sulfides of the considered elements, assuming that $a_{Me} = a_{MeS} = a_{MeO}$. Fig.2.

Based on the results shown in Fig.2. it can be concluded that the sulfides and oxides of Zn, Co, Ni, Pb and Cu are stable under the conditions of sulphide copper concentrate smelting, therefore these elements are present in the slag melt in both forms. On the other hand, Sb, As, Bi and Ag are stable in the metallic form.

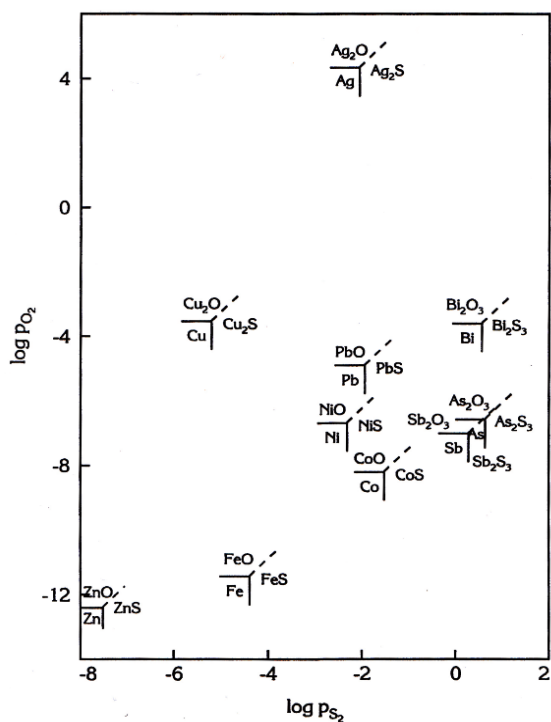


Fig.2. Diagram of the sulfur - oxygen potential for different metal - sulfur - oxygen systems at 1200 °C.

Based on Ellingham diagram of sulfide stability for considered elements (Fig. 3.), it can be observed that only ZnS is stable among other sulfides present in the matte (Cu₂S - FeS) under the conditions of sulphide copper concentrate smelting, which indicates that only ZnS can be expected in the matte melt, while the presence of other elements in the matte can be explained by their solubility in the metallic form, building solutions with Cu and Fe - the most abundant components in the matte.

Due to the presence of the chlorine in the matte, it can be assumed that a portion of the elements, present in the matte, are in the form of chlorides. The content of Au in the matte in this study is determined within the

limits of 0.003 – 0.006%, while it was not registered in the slag. Also, the content of Bi in the matte was within the limits of 0.03 – 0.06%, while only trace amounts of it were registered in the slag. The Te content in the matte was within the limits of 0.01 – 0.015%, and only trace amounts were found in the slag. Therefore, the distribution coefficient for these three elements was not calculated.

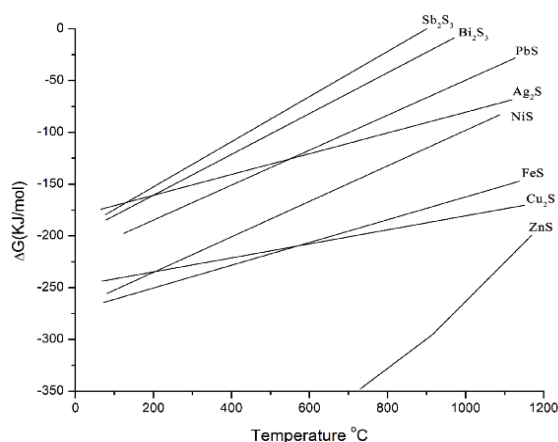


Fig.3. Ellingham diagram of stability for some sulphide forms.

The Fig. 4. shows the values for the distribution coefficient $L^{S/M}_{Me}$ for the copper content in the matte of 36.31% Cu and 42.12% Cu. Obtained results indicate that the distribution coefficient $L^{S/M}_{Me}$ increases in the Cu – Ag – Se – Ni – As – Pb – Sb – Zn series, while the Au, Bi i Te almost completely concentrate in the matte. This trend applies to both contents of copper in the matte. $L^{S/M}_{Me}$ for Zn, Sb, Pb and As, has the smallest impact of the content of copper in the matte, while the influence of copper content on the $L^{S/M}_{Me}$ for Ag, Se and Ni is much stronger.

Copper matte represents a ternary system

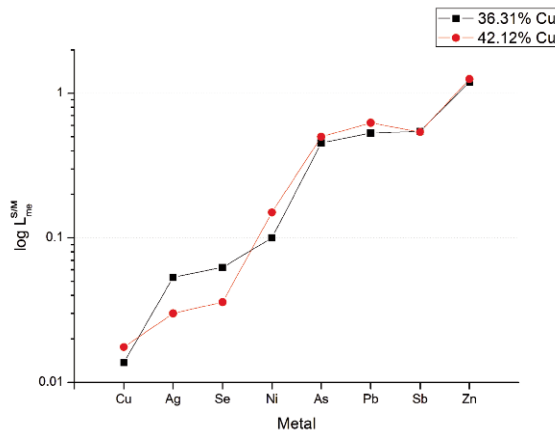


Fig. 4 Distribution of $L^{S/M}_{Me}$ coefficient for certain elements

Cu-Fe-S, according to its composition, or a binary system of two sulfide $Cu_2S - FeS$. In the investigated system Cu content was within the range of 36.31 to 42.12% Cu, 34.91 to 29.44% Fe and 26.13 to 25.45% S. Increase of Cu content in the matte leads to Fe content decreases, which increases the likelihood of dissolution of the present

accompanying components i.e. the creation of the binary systems Cu - Me. Fig. 5 shows the dependence of $L^{S/M}_{Me}$ on the copper content in the matte. The results obtained under industrial conditions showed that with increase of the copper content in matte $L^{S/M}_{Me}$ increases in the case of Cu, Zn and Pb; decreases in the case of Ag and Se, and remains almost the same in the case of Ni, Sb and As.

Thermodynamic explanation of the certain elements behavior in the studied system can be defined via the theory of real solutions and Ellingham diagrams of stability of sulphides, under the conditions of sulphidic copper concentrate smelting.

The thermodynamic properties of real solutions are examined the best by means of the concept of excess functions.

The excess Gibbs energy of mixing is equal to the difference between actual Gibbs energy of mixing of solution and Gibbs energy of mixing which the solution would

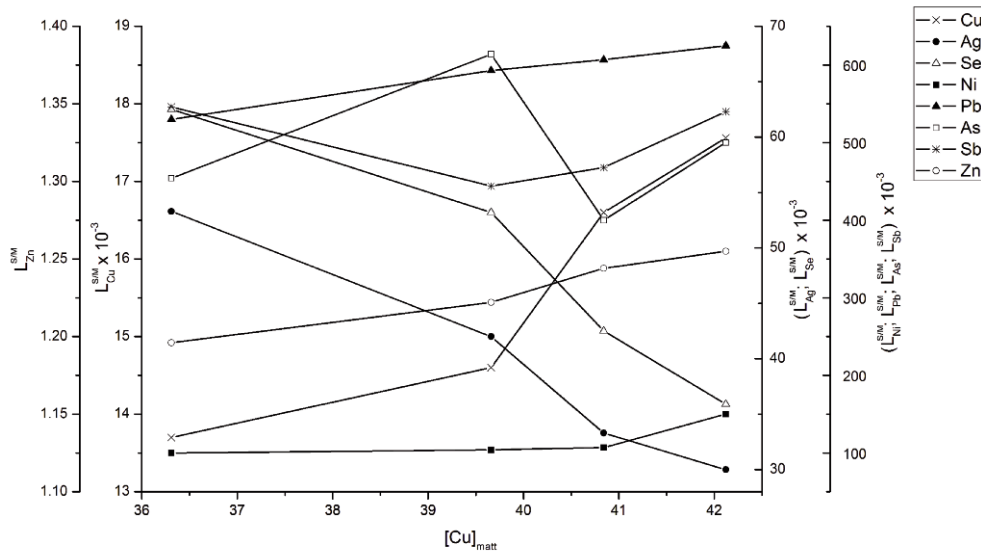


Fig. 5 Dependence of $L^{S/M}_{Me}$ on the copper content in the matte.

have if being ideal:

$$\Delta G^{xs} = \Delta G^{mix} - \Delta G^{id} \quad (4)$$

Negative value of ΔG^{xs} in i - j binary system corresponds to the situation when the i - j bond energy is more negative than both i - i and j - j bond energies, and this causes the tendency toward “ordering” in the solution, in which the i atoms attempt to only have j atoms as nearest neighbors and vice versa. Negative ΔG^{xs} thus indicates a tendency toward the formation of compounds between the two components. Conversely, positive ΔG^{xs} occurs when i - j bond energy is less negative than both i - i and j - j bond energies, and thus causes a tendency toward phase separation or “clustering” in the solution.

The basic form of the equation of excess Gibbs energy of mixing for binary i - j solution is:

$$\Delta G^{xs} = x_i x_j L_{ij} \quad (5)$$

If the regular-solution parameter L_{ij} is temperature independent constant, the thermodynamic solution model is called regular. However, the binary regular-solution term is often not enough to describe the real solution behavior. It is usually extended by using following equation:

$$L_{ij} = \sum_{\nu=0}^k (x_i - x_j)^\nu L_{ij} \quad (6)$$

This form of the composition dependence for a binary interaction is generally known as a Redlich-Kister (RK) power series. The parameters ${}^\nu L_{ij}$ in the RK series are usually temperature-dependent:

$${}^\nu L_{ij} = {}^\nu a_{ij} + {}^\nu b_{ij} T \quad (7)$$

The optimized values of RK parameters for the liquid phase, published in literature, were used for the calculation of ΔG^x at 1200 °C in binary Cu-X and Fe-X systems. The optimized RK parameters for the liquid phase in the Cu-X (X = Ag, Au, Bi, Pb, Sb, Zn, Ni, Se) systems were taken from the COST 531 thermodynamic database [20]. For the Fe-X (X = Zn, Pb, Sb, Bi, Ni, As) systems RK parameters were published in the reference [21], Fig. 6.

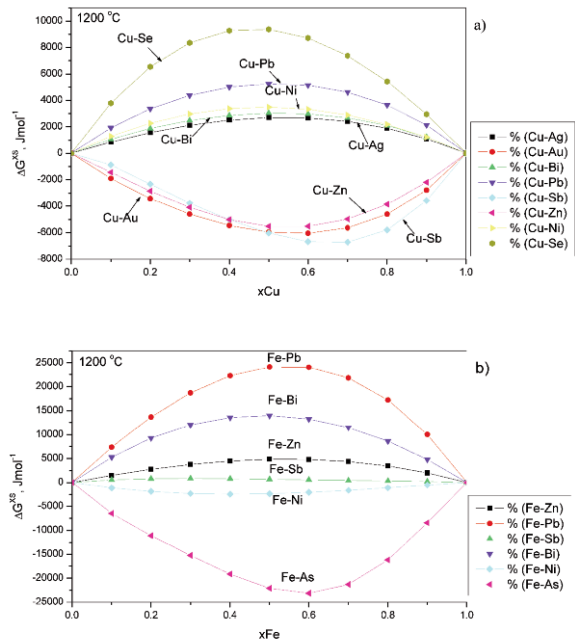


Fig.6. Dependence of ΔG^{xs} for Cu – Me (a) and Fe – Me (b) at the temperature of 1200°C.

Acquired results indicate that the entire Au contents concentrates in the matte, can be explained due to high negative values of ΔG^{xs}_{Cu-Au} . Also the Bi in the matte builds a nearly ideal solution with Cu, because ΔG^{xs}_{Cu-Bi} tends to zero. Also, the $L_{Ag}^{S/M}$

decrease can be explained with the value of ΔG^{xs}_{Cu-Ag} which tends to zero, due to which this system approaches the position of the ideal solutions, in the concentration area of the considered systems. This also applies to the $L^{S/M}_{Ni}$ which does not vary much with the increasing copper content in the matte. The increase in $L^{S/M}_{As}$ with increasing Cu content in the matte can be explained by the fact that the content of Fe decreases in the matte, while in the system Fe-As change of $\Delta G^{xs}_{Fe-As} < 0$. The increase in $L^{S/M}_{Cu}$ with increasing copper content in the matte shows an increase in Cu content in the slag due to the higher Cu content in the matte droplets captured in the slag, Fig.1. [7]

Dependences of variations of $L^{S/M}_{Me}$ on the copper content in matte for Pb, Zn, Se and Sb are complex, depend on a number of parameters and cannot be explained only on the basis of results of ΔG^{xs}_{Cu-Me} and ΔG^{xs}_{Fe-Me} shown in Fig. 6.

4. Conclusion

The distribution of Cu, Au, Ag, Ni, Se, Zn, As, Sb, Pb and Bi between the slag and the matte, during the process of sulphide copper concentrate smelting, in addition to dependence on the composition of the slag, also depends on the content of copper in the matte. The decrease of the distribution coefficient $L^{S/M}_{Me}$ with the increase of the Cu content in matte for Ag is caused by the values of ΔG^{xs} for the system Cu-Ag, which tends to zero, in other words these elements build ideal solutions. Similar behaviors have Au, Bi, Ni as well, the elements which concentrate in the matte due to the tendency of these elements to build approximately

ideal solutions with the copper. The increase in $L^{S/M}_{Me}$ for Pb, Zn, Se and Sb is much more complex and cannot be explained with available data. Explanation of changes in $L^{S/M}_{Me}$ for these elements requires additional research.

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Reference

- [1] A.K. Biswas, W.G. Davenport, Extractive metallurgy of copper 3rd.edn, Pergamon Press, Exeter, 1994.
- [2] R.R. Moskalyk, A.M. Alfantazi, Minerals Engineering, 16 (10) (2003) 893.
- [3] I. Mihajlović, Đ. Nikolić, N. Štrbac, Ž. Živković, Serbian Journal of Management, 5 (1) (2010) 39.
- [4] N. Mitevski, The influence of technological parameters and the interface phenomena on the copper losses with the slag, PhD Thesis, Belgrade University, Technical Faculty in Bor, 2000 (in Serbian).
- [5] N. Mitevski, Ž. Živković, J. Marinković, Rudy i metale neželazne, 45 (8) (2000) 435.
- [6] N. Mitevski, Ž. Živković, J. Min. Metall. Sect. B-Metall., 38 (1-2) B (2002) 93
- [7] Z. Zivkovic, N. Mitevska, I. Mihajlovic, D. Nikolic, Miner. Metall. Process., 27 (3) (2010) 141.
- [8] I. Djuric, P. Djordjevic, I. Mihajlovic, D. Nikolic, Z. Zivkovic, J. Min. Metall. Sect. B-Metall., 46 (2) (2010) 161.

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- [9] K. Fageurland, *Acta Polytech. Scand., Chem. Technol. Ser.*, No.258, 1998.
- [10] B. Gorai, R.K. Jana, Premchand, *Resour. Conserv. Recy.*, 39 (4) (2003) 299.
- [11] C. Shi, C. Meyer, A. Behnood, *Resour. Conserv. Recy.*, 52 (10) (2008) 1115.
- [12] D. Nikolić, N. Milošević, I. Mihajlović, Z. Živković, V. Tasić, R. Kovačević, N. Petrović, *Water, Air, Soil Pollut.*, 206 (1-4) (2010) 369.
- [13] W.-h. Gui, L.-y. Wang, C.-h. Yang, Y.-f. Xie, X.-b. Peng, *T. Nonferr. Metal. Soc.*, 17 (5) (2007) 1075.
- [14] P. Djordjević, I. Mihajlović, Ž. Živković, *Serbian Journal of Management*, 5(2) (2010) 189.
- [15] I. Mihajlović, N. Štrbac, P. Djordjević, A. Ivanović, Ž. Živković, *Serbian Journal of Management*, 6 (2) (2011) 135.
- [16] H. Jalkanen, J. Vehviläinen, J. Poijärvi, *Scand. J. Metall.*, 32 (2) (2003) 65.
- [17] I. Imris, M. Sánchez, G. Achurra, *Miner. Process. Extract. Metall.*, 114(3) (2005) 135.
- [18] A. Yazawa, *Can. Metall. Q.*, 13 (3) (1974) 443.
- [19] M. Nagamori, P.J. Mackey, *Met. Trans.*, 8B (1977) 353.
- [20] A.T. Dinsdale, A. Watson, A. Kroupa, A. Zemanova, J. Vrestal and J. Vizdal, *COST 531 Database Version 3.0*, (2008).
- [21] SGTE Solution Database.
<http://www.sgte.org/>.