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Hot Rolling Process Optimization for Hot Shortness Problem

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Tramp element is defined as elements cannot be refined in conventional steel refinement methods due to thermodynamic nature of element. These elements cannot be oxidized in steel and refined with oxidization – slag formation method due to lower oxygen affinity than iron. Tramp elements accumulate in steel within every recycling. These elements are; Cu, Ni, Sn, Sb and As. The problem with tramp elements is they have detrimental effects on steel properties. Hot shortness is a problem occurs in tramp element containing steel especially with copper. During the annealing enrichment of copper under the surface occurs because of selective oxidation of iron on surface. Enriched copper beneath the mill scale transforms to liquid form. Liquid copper migrates to austenite grain boundaries then with mechanical force of rolling process causes cracks on steel surface.

This study is aimed to explain and understand hot shortness behaviour under different circumstances. In this study copper is artificially alloyed to steel to simulate hot rolling performance of steel with tramp element containing steel. Hot rolling process is carried out for two different annealing temperature and effects of S, P and Mn alloying is investigated. Crack formation and crack numbers are calculated and optical and SEM imaging is done for crack behaviour observation. Results promoted that annealing treatment and alloying can be effective against hot shortness.

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1. Introduction

Steel is the most recycled and produced metal worldwide.[1] Recycling of steel is promoted through the world since recycling of material has lower carbon impact and economically feasible. Carbon footprint decrease and environmental challenges for steel is shaping steel producing techniques and trends for steel producers. [2,3] Increasing steel demand and production amounts force producers to develop more flexible processes. Main concern of steel recycling process is the quality of scrap to be recycled. One of the main factors effecting scrap quality and end-product properties is the chemical composition of scrap. Chemical composition of scrap directly effects end-product quality.[4] Tramp element existence in scrap is one of the problems regarding to chemical composition. Tramp element is defined as elements cannot be refined from steel with conventional oxidative refinement processes. These elements has lower oxygen affinity than iron thus oxidation of these elements in steel media is thermodynamically impossible.[5] These elements are; Cu, Ni, Sn, Sb and As.

Hot shortness is macro crack formation on steel surface in hot rolling process. Main cause of hot shortness is having tramp elements in steel, especially Cu. Hot shortness mechanism has two main step; segregation of Cu between austenite grain boundaries, formation of intergranular crack with mechanical force of hot rolling. [6–9] Hot shortness mechanism is widely studied by various researches yet still provides promising research topics. Copper segregation is linked to oxidation of steel. [10,11] Oxidation of Fe on steel surface forms oxide scale meanwhile copper remains in metallic form and has tendency to diffuse into metallic Fe. Cu that can pass the threshold of critical segregation point and penetrate through austenite grain boundaries. That phenomenon causes macro cracks due to decreasing grain boundary cohesion between austenite grains.[6,12]

Several studies are done to decrease the detrimental effects of Cu on steels. General point of view is to refinement of Cu and other tramp elements with different techniques. Cyclic oxidation[13], oxychlorination[14], different slag systems[15–20] are studied to refine Cu and other tramp elements from steel.

2. Experimental

Slabs of different Cu amount with alloying addition are prepared by casting method. 50 KW capacity of induction furnace is used for smelting 50 kilograms of steel. Molten steel is alloyed with Cu and casted into resin mould. After casting of Cu alloyed steel S, P and Mn is alloyed to molten steel and casted respectively after every alloying addition. Casted slabs cooled down naturally to room temperature in air. Chemical analysis of samples is done with Optic Emission Spectroscopy (OEM).
Casted slabs are annealed at 1000 and 1200 oC for 30 minutes then hot rolled with rolling simulator machine with capacity of 50 tonnes of force. Previous works showed that increasing annealing time increases oxidation of material therefore increases copper segregation.[10,21] Hot rolling mechanical forces and end of process temperatures of slabs are collected. Hot rolled samples are evaluated in case of crack numbers and crack lengths. Crack number evaluation is done with calliper precision of 0.05 mm. Crack evaluation process is given in Figure 1. Optical microscopy and Scanning Electron Microscopy (SEM) imaging of samples are done for selected samples. Thermodynamic calculations are done with HSC 6.1 and FactSage 7.3 softwares.

***Figure 1**. Determination of Surface Edge Cracks with Calliper.*

3. Results and Discussion

Chemical analysis of samples is done with OES. Chemical analysis results are given in Table 1. Analysis shows that every alloying step diluted previous alloying element. Samples are named as Cu, Cu-S, Cu-P and Cu-Mn due to last alloyed element to steel.

Table 1. Chemical Composition of Samples.

Sample	**C %**	**Mn %**	**Si %**	**S %**	**P %**	**Cr %**	**Cu %**	**Ni %**	**O %**
Cu	0,369	0,54	0,19	0,01	0,015	0,11	2,82	0,09	0,02
Cu-S	0,362	0,56	0,19	0,02	0,60	0,12	2,84	0,09	0,02
Cu-P	0,313	0,87	0,16	0,33	0,38	0,12	2,96	0,09	0,04
Cu-Mn	0,443	2,83	0,18	0,24	0,32	0,11	2,58	0,09	0,02

Carbon amount of castings are in the range of mid-carbon steel. Ferro-phosphorus had some manganese and copper thus increased the manganese and copper amounts in Cu-P casting. On the other hand ferro-manganese that is used in manganese alloying was high carbon ferromanganese and increased carbon amount of steel while diluting S, P and Cu.
Crack numbers and total crack length is measured with calliper. Results are given in Figure 2 and 3. It can be seen from graphs 1000 oC rolling temperature causes less cracks with better surface condition. Rolling below the Cu melting point limits the segregation of copper on the surface while increasing need of force for rolling temperature. Hot rolled samples after annealed at 1200 oC have higher crack number with longer lengths. Samples rolled at 1000 oC show that sulphur and phosphorus has limited effect on both crack length and crack numbers. On the other hand Mn decreases crack numbers while crack length increased drastically. This is the result of manganese effect on strain hardening. Manganese has an effect of increasing austenite area of iron as an alloying element. Copper has better solubility in austenite than ferrite thus increasing austenite amount in steel decreases chance of crack formation. Strain hardening on the contrary intensify cracking by the effect of manganese.

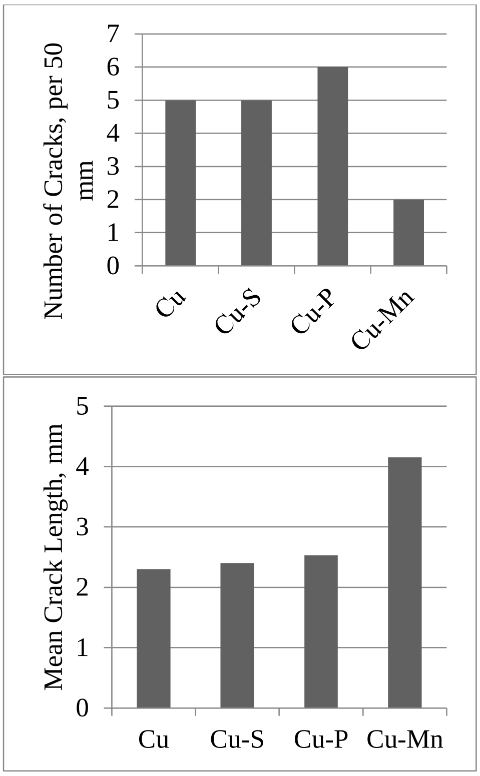

Figure 2. *Crack Number of Slabs and Mean Crack Length after Hot Rolling at 1000 ºC.*

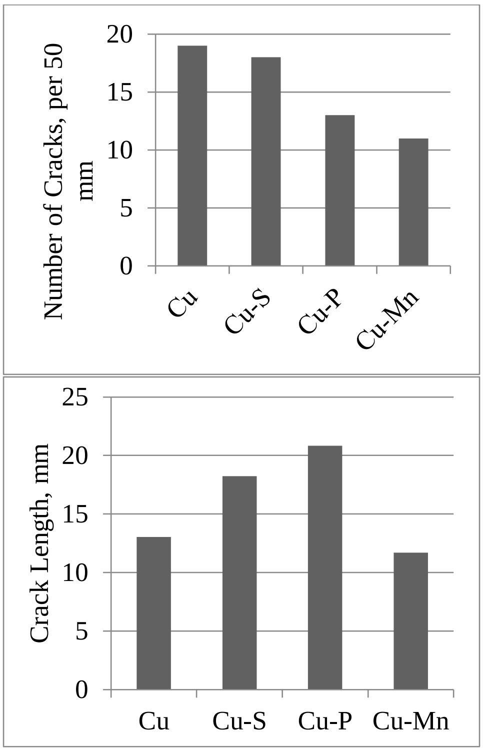

Figure 3. *Crack Number of Slabs and Mean Crack Length after Hot Rolling at 1200 ºC.*

Number of cracks is decreased with alloying elements at 1200 ºC. Sulphur and phosphorus is known for affinity to bond with Cu rather than iron. Previous studies proved that sulphur and phosphorus bond with copper and decreases chance of copper segregation. [19,22–26] crack numbers decreased nevertheless mean crack lengths are increased. Manganese increases austenite area in binary phase diagram. Detrimental effect of manganese is eliminated with increased rolling temperature. Higher rolling temperature decreases need of rolling force and strain hardening effect. Hence manganese alloyed slab has the best performance at 1200 ºC.

SEM images of samples are collected with Back Scattered Electron technique. EDS analysis and EDS mapping are applied to sample. Cu-S sample is imaged to observe possible Cu segregations under surface and crack propagation areas. SEM image is given in Figure 4 and EDS mapping result is given in Figure 5. EDS analysis of spots are given in Table 2. EDS spot analysis along with mapping shows that Cu segregates accumulated through crack region. Dark areas of image are resin mould.

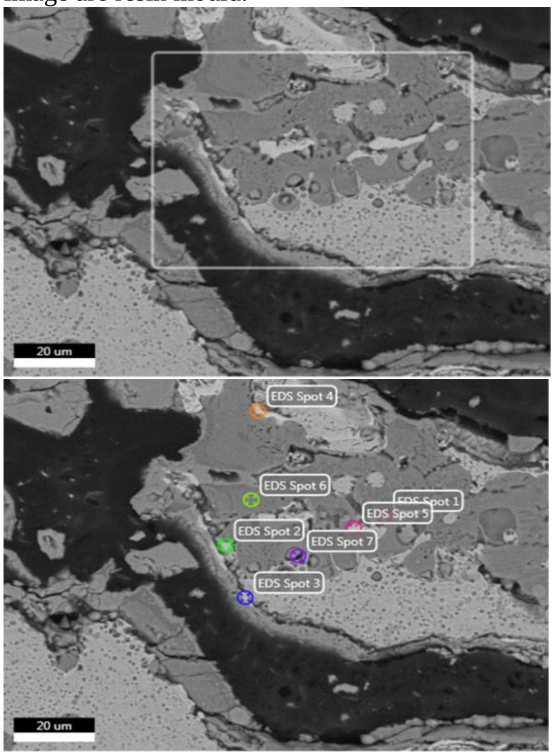

Figure 4. *SEM Image of Cu-S Sample with Mapping Area and EDS Spots.*

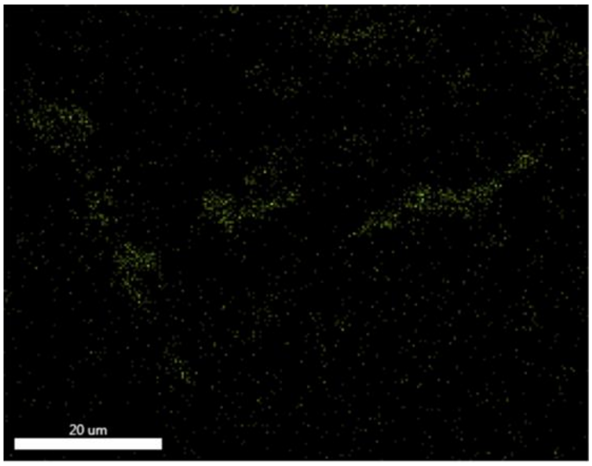

Figure 5. *EDS Mapping of Sample.*

Table 2. EDS Spots Analysis Results.

Spot	**Fe%**	**Cu%**	**O%**	**Ni%**	**Si%**
1	12.03	86.70	1.27	-	-
2	11.64	83.52	1.42	3.41	-
3	19.28	76.82	3.90	-	-
4	18.44	75.16	1.54	4.86	-
5	11.84	86.66	1.50	-	-
6	57.99	-	30.87	-	11.14
7	50.49	49.51	-	-	-

Analysis showed that Cu accumulated under surface of mill scale. Crack propagation started copper enriched areas. Copper enrichment is generally has low iron content. Mill scale observation is done and Cu particle is encapsulated in mill scale. That results shows copper enrichment starts with oxidation of iron on surface. If enough time is given to material segregated copper migrates to material surface then to grain boundaries. Image is given in Figure 6. Rectangle on the image shows mapping area of EDS.

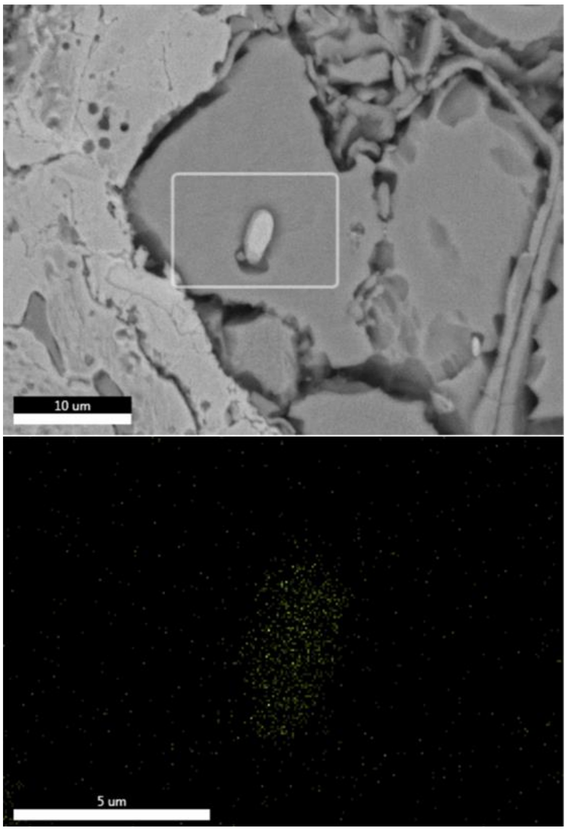

Figure 6. *SEM and EDS Mapping of Mill Scale. (Green indicates Cu)*

Optical microscopy images show that crack propagation points on surface have copper segregation for 1200 ºC annealed samples. 1000 ºC annealed samples have better surface quality without any copper segregation. Figure 7 shows Cu-Mn sample for both 1000 and 1200 ºC annealed condition. 1200 ºC sample has copper segregation on crack propagation point. Copper segregation goes parallel to crack line.

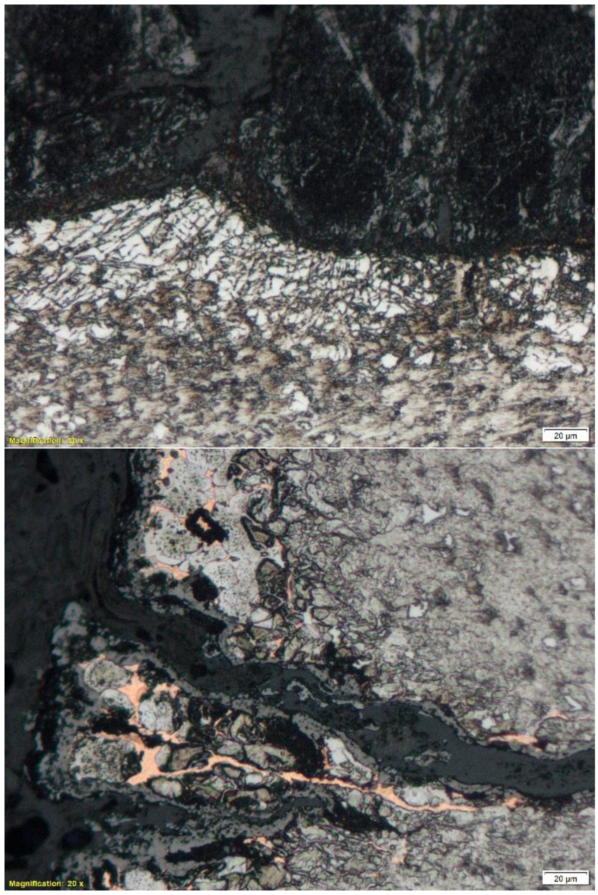

Figure 7. Optical Microstructure of Cu-Mn samples 1000 ºC (left) 1200 ºC (right).

4. Thermodynamic Calculations

Thermodynamic calculations are based on copper and alloying elements relation. Sulphur and phosphorous are known for affinity to copper. On the other hand manganese is an austenite enhancer furthermore increases copper solubility in steel. Ellingham diagram of Cu-Fe-S and Cu-Fe-P is given in Figure 8 and 9 respectively. Fe-2.8Mn – Cu binary phase diagram is given in Figure 10.

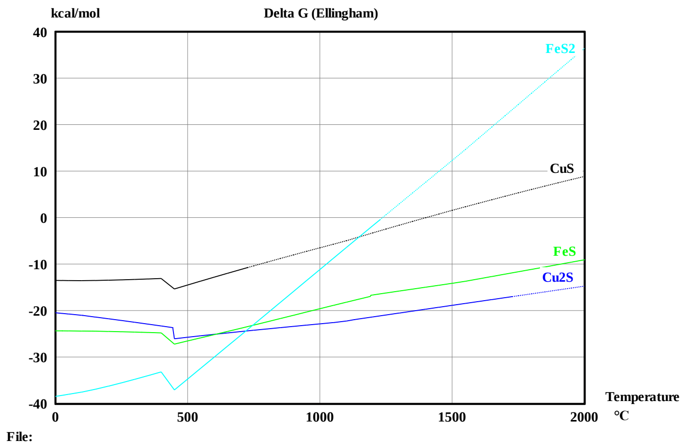

Figure 8. *Ellingham Diagram of Cu-Fe-S.*

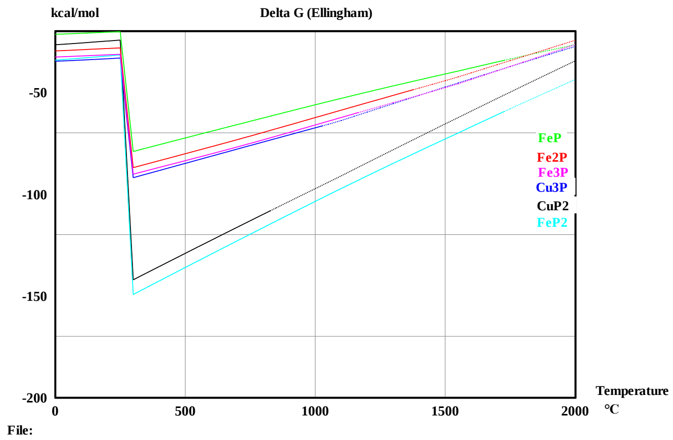

Figure 9. *Ellingham Diagram of Cu-Fe-P.*

Ellingham diagrams showed that Cu affinity to S is the highest and Cu_2S is the most stable phase for sulphur added condition. Phosphorus on the other hand tends to bond with Fe in FeP_2 form. CuP_2 has also negatively high free energy and is possible to form in steel.

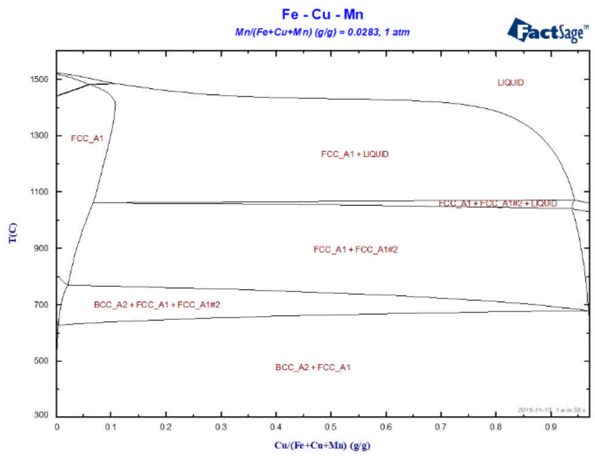

Figure 10. *Fe-2.83 Mn-Cu binary phase diagram.*

Binary phase diagram of Fe-2.83 Mn-Cu shows additional two FCC phases below 700 °C. Manganese presence in steel increases austenite fraction at lower temperatures. Austenite is known for higher copper solubility than ferrite. Formation of another solid solution phase in this system creates chance for decreasing copper segregation.

5. Conclusion

Copper is defined as tramp element for steel and has detrimental effect on mechanical properties. Alloying elements are found to be decrease copper effect on hot shortness. Sulphur and phosphorus is aimed to decrease free copper amount in steel with formation of copper based compounds. Nevertheless these elements have also detrimental effects on steel mechanical properties. Manganese is found to be effective against hot shortness problem with increasing austenite stable region area. Copper solubility increase decreases chance of segregation of element in steel. On the other hand manganese increases strain hardening at lower rolling temperatures result in decreasing in crack number while increasing crack length. 1000 °C rolled samples shows S and P has no significant effect on both crack number or crack length while Mn decrease crack number with increasing crack length. S and P decreases crack numbers at 1200 °C on the contrary of increasing crack length. This result is related to relation between iron and these elements among the copper. Manganese on the other hand has the best result in means of crack number and length at 1200 °C. As a conclusion manganese is found to a possible candidate for developing an optimum hot rolling process of tramp element containing steels. Decreasing of rolling temperature decreases cracking on slab surface and should be considered as another helpful instrument against hot shortness.

References

[1] Björkman B, Samuelsson C. Recycling of Steel. Handb Recycl State-of-the-Art Pract Anal Sci 2014:65–83. doi:10.1016/B978-0-12-396459-5.00006-4.

[2] Sym STEEL, Um POSI, Brankley L, Anderson J, Camci L. SUSTAINABILITY AND LIFE CYCLE ANALYSIS IN – A CASE Sustainability and Life Cycle Analysis in Construction Materials Certifications – A Case Concrete [2]One Planet Limited , [3]Previously of Thinkstep Limited , Now of Construction LCA • United Kingdom 2011:10–7.

[3] Knight D, Knight D, Steel K, Change C, Reductions COE. Can Steel Production Be Sustainable ? CAN STEEL PRODUCTION BE SUSTAINABLE ? One Planet Limited • United Kingdom 2018:2–9.

[4] Nakamura S, Kondo Y, Matsubae K, Nakajima K, Tasaki T, Nagasaka T. Quality- and dilution losses in the recycling of ferrous materials from end-of-life passenger cars: Input-output analysis under explicit consideration of scrap quality. Environ Sci Technol 2012;46:9266–73. doi:10.1021/es3013529.

[5] Rod O, Becker C, Nylén M. Opportunities and dangers of using residual elements in steels. Lit Study 2006;819.

[6] Yin L, Sridhar S. Effects of residual elements arsenic, antimony, and tin on surface hot shortness. Metall Mater Trans B Process Metall Mater Process Sci 2011;42:1031–43. doi:10.1007/s11663-011-9528-z.

[7] Imai N, Komatsubara N, Kunishige K. Effects of Cu and Other Tramp Elements on Steel Properties. Effect of Cu and Ni on Hot Workability of Hot-rolled Mild Steel. ISIJ Int 2008;37:224–31. doi:10.2355/isijinternational.37.224.

[8] Jiang Y, Xie C. Evaluation model of susceptibility

to Cu hot shortness of Cu-containing LC steel. IOP Conf Ser Mater Sci Eng 2017;207. doi:10.1088/1757-899X/207/1/012098.

[9] Kunishige K, Hatano M. Surface Hot-Shortness of Steels Induced by a Small Amount of Copper and Tin from Scrap Steels and its Suppression Methods. Mater Sci Forum 2009;539–543:4113–8. doi:10.4028/www.scientific.net/msf.539-543.4113.

[10] Yeşiltepe S, Şeşen MK. No Title. High Temp. Oxid. Kinet. Cu Bear. Carbon Steel, 2019, p. 118–22.

[11] Kondo Y. Effect of Atmospheric Conditions on Copper Behaviour during High Temperature Oxidation of a Steel Containing Copper. ISIJ Int 2007;47:1309–14. doi:10.2355/isijinternational.47.1309.

[12] Webler BA, Sridhar S. Evolution and Distribution of the Copper-rich Phase during Oxidation of an Iron–0.3wt%Copper Alloy at 1150°C. ISIJ Int 2008;48:1345–53. doi:10.2355/isijinternational.48.1345.

[13] Shin SM, Lee DW, Ha SA, Wang JP. Study of Cyclic Oxidation for Copper Removal from Solid Ferrous Scrap in End-of-Life Vehicle (ELV). Adv Mater Res 2013;699:869–74. doi:10.4028/www.scientific.net/amr.699.869.

[14] Tee JKS, Fray DJ. Separation of copper from steel. Ironmak Steelmak 2006;33:19–23. doi:10.1179/174328106x80028.

[15] Ono-nakazato H, Taguchi K, Kawauchi D, Usui T. Separation of Fe and Sn – Cu Phases in an Fe – Sn – Cu – B System Sn-rich 2006;47:864–7.

[16] Sasaki N, Uchida Y-I, Miki Y-J, Matsuno H. Fundamental Study of Sn Removal from Hot Metal by NH_3 Gas Blowing. Tetsu-to-Hagane 2015;102:17–23. doi:10.2355/tetsutohagane.tetsu-2015-056.

[17] Sasaki N, Uchida Y, Kishimoto Y, Miki Y. Fundamental Investigation on Removal of Copper from Molten Iron with Na 2 CO 3 -FeS Fluxes promoting utilization of scrap procured in the market and reducing energy 2 . Principle and Target of Cu Removal by Sulfidation 2012;55:1–6.

[18] Zhang J, Qi YH, Yan DL, Xu HC. A New Technology for Copper Slag Reduction to Get Molten Iron and Copper Matte. J Iron Steel Res Int 2015;22:396–401. doi:10.1016/S1006-706X(15)30018-2.

[19] Yamaguchi K, Ohara T, Ueda S, Takeda Y. Copper Enrichment of Iron-Base Alloy Scraps by Phase Separation in Liquid Fe-Cu-P and Fe-Cu-P-C Systems. Mater Trans 2006;47:1864–8. doi:10.2320/matertrans.47.1864.

[20] WANG J jun, GUO S xing, ZHOU L, LI Q. Slag for Decopperization and Sulphur Control in Molten Steel. J Iron Steel Res Int 2009;16:17–21. doi:10.1016/S1006-706X(09)60021-2.

[21] Yeşiltepe S, Şeşen MK. No Title. Hot Shortness Mech. Mill Scale Charact. Low Carbon Steels, Karabük: 2019, p. 221.

[22] Liu Z, Kobayashi Y, Nagai K, Yang J, Kuwabara M, Ii T. Morphology Control of Copper Sulfide in Strip Casting of Low 2006;46:744–53.

[23] Liu Z, Kobayashi Y, Nagai K. Crystallography and Precipitation Kinetics of Copper Sulfide in Strip Casting Low Carbon Steel. ISIJ Int 2008;44:1560–7. doi:10.2355/isijinternational.44.1560.

[24] Urata K, Kobayashi Y. Precipitation Mechanism of Copper Sulfides in Solid Iron 2016;16:342–7.

[25] Kim SI, Chin KG, Yoon JB. Precipitation Hardening with Copper Sulfide in Cu Bearing Extra Low Carbon Steel Sheet. ISIJ Int 2009;49:109–14. doi:10.2355/isijinternational.49.109.

[26] Cha W-Y, Kobayashi Y, Susa M, Endo R, Urata K. Growth Rate of Copper Sulfide Precipitates in Solid Low Carbon Steel. ISIJ Int 2015;55:103–8. doi:10.2355/isijinternational.55.103.