JOM, Vol. 70, No. 8, 2018
https://doi.org/10.1007/s11837-018-2965-2

TECHNICAL COMMUNICATION

Recovery of Gold and Silver from Secondary Sources of Electronic Waste Processing by Thiourea Leaching

HYUNJU LEE,[1] EMILY MOLSTAD,[1] and BRAJENDRA MISHRA[1,2]

1.—Mechanical Engineering, Worcester Polytechnic Institute, Worcester, MA 01609, USA.
2.—e-mail: bmishra@wpi.edu

Fine materials, such as flue dust, generated during processing of electronic waste (e-waste) contain valuable metal resources, such as Au and Ag. However, recovery of valuable metals from this flue dust has not been extensively studied. In this study, a leaching process was investigated for effective recovery of Au and Ag from flue dust. In particular, thiourea was used as leaching reagent to replace cyanide, which has environmental problems. The effects of various parameters on the process, such as leaching time (1–10 h), thiourea concentration (20–60 g/L), and pulp density (20–100 g/L) as well as reaction temperature (20–60°C), were systematically examined. One- and two-step leaching methods were proposed to recover Au and Ag, respectively. Au and Ag leaching efficiencies of about 90% and 100% were obtained by one-step thiourea leaching. However, metals such as Fe and Al were also dissolved together. In the two-step process, Fe and Al were dissolved using H_2SO_4 as a first step, then Au and Ag were recovered using thiourea leaching. Using this two-step process, Au and Ag were dissolved at higher purity than when using the one-step leaching process, achieving leaching efficiencies of about 98% and 100%, respectively. This investigation will lead to a cost-effective method for recovering precious metals from secondary waste.

INTRODUCTION

The life cycle of electrical and electronic equipment has shortened as a consequence of advancement in technology. This has resulted in generation of large quantities of electronic waste (e-waste).[1,2] E-waste contains harmful components, but also valuable metals such as Au, Ag, and Cu. For this reason, e-waste recycling is important in terms of environmental protection and valuable metal recovery.

Recently, some researchers have reported studies on recycling of e-waste based on hydrometallurgy.[3–7] Leaching is a process for extracting soluble constituents from a solid by using a solvent in a hydrometallurgical process. The most common leaching agent used in recovery of precious metals is cyanide.[8] Although cyanide is a very efficient product in industry, it is highly toxic and thus harmful to human health and the environment. Therefore, many studies have evaluated other solvents to substitute this toxic chemical.[9]

Various reagents such as halide, thiosulfate, and thiourea can replace cyanide.[8–10] Among these, research on thiourea as Au extraction agent has shown considerable promise.[11] However, it is more expensive than cyanide, and the Au recovery step requires further development.[10] The thiourea leaching process is currently at a low research level, but it may be expected that it will become economically feasible following extensive research.

Fine materials, such as flue dust, are generated in smelters or metallurgical furnaces. Some researchers have investigated recovery of valuable metals from Cu smelter slag using leaching processes.[12,13] However, studies on leaching of flue dust generated during the smelting process of e-waste are not well known.

In this study, we investigated two thiourea leaching processes for effective recovery of Ag and Au from flue dust. The effects of various parameters on the process, such as leaching time (1–10 h), thiourea concentration (20–60 g/L), pulp density (20–100 g/L), and leaching temperature (20–60°C), were sys-

Table I. Composition analysis of fine material from e-waste

Sample $< 75\ \mu m$	Composition										
	Ag (ppm)	Au (ppm)	Cu (wt.%)	Pb (wt.%)	Zn (wt.%)	Ni (wt.%)	Co (wt.%)	Fe (wt.%)	Mn (wt.%)	Al (wt.%)	Ca (wt.%)
	2111	141	1.7	0.1	1.6	0.9	0.1	13.3	0.9	6.0	4.1

tematically examined. Finally, one- and two-step leaching processes were performed, and the Au and Ag leaching efficiencies compared for effective recovery.

EXPERIMENTAL PROCEDURES

Fine materials were provided by an e-waste recycling company in Europe. To optimize the effective recovery process, size separation (RX-29, W.S. Tyler) was performed as a pretreatment process. The as-received sample ($< 75\ \mu m$) was fused with a lithium borate mixture (40 wt.% lithium tetraborate, 60 wt.% lithium metaborate) at 1100°C for 1 h. After this borate fusion process, the melt was dissolved in HNO_3 for inductively coupled plasma optical emission spectrometry (ICP-OES) analysis (Optima 8000, PerkinElmer). This fusion process has several advantages, viz. minerals are readily dissolved, no pressure vessel is needed, and clear aqueous solution is obtained for a variety of analytical procedures.[14]

H_2SO_4 (95–98%, J. T. Baker), thiourea (> 99.0%, Sigma-Aldrich), and H_2O_2 (30 wt.%, Sigma-Aldrich) were used as leaching reagents. During leaching, the solid/liquid content was varied from 20 g/L to 100 g/L and the bath temperature from 20°C to 60°C. A magnetic stirring bar was also used to mix the solution during leaching at fixed speed of 250 rpm. One- and two-step leaching processes were proposed to recover Au and Ag. After leaching, the solid residue was separated from the leachate by vacuum filtration, and the solid residue was dried in an oven (110°C) for about 2 h. As for the initial sample, the solid residue was prepared for analysis using the fusion process. The leachate and solid residue were analyzed by ICP-OES.

RESULTS AND DISCUSSION

Initial Characterization of As-Received Sample

Table I presents the results of the ICP-OES analysis, including each element in the composition. Major elements present in the sample were Fe and Al with content of 13.3 wt.% and 6 wt.%, respectively. The sample also contained valuable metals such as Au (141 ppm) and Ag (2111 ppm). Based on these ICP-OES results, two types of leaching process were performed. The first method was thiourea leaching to recover Au and Ag as a one-step process. The second (two-step) method was leaching to recover base metals (Fe, Al) in a first step then valuable metals (Au, Ag) in a second step.

One-Step Leaching Process for Recovery of Au and Ag

Thiourea leaching was performed for recovery of Au and Ag. Fe(*III*), H_2O_2, and $Fe_2(SO_4)_3$ are well known as the most suitable oxidants for thiourea leaching of Au.[15] Some researchers have used

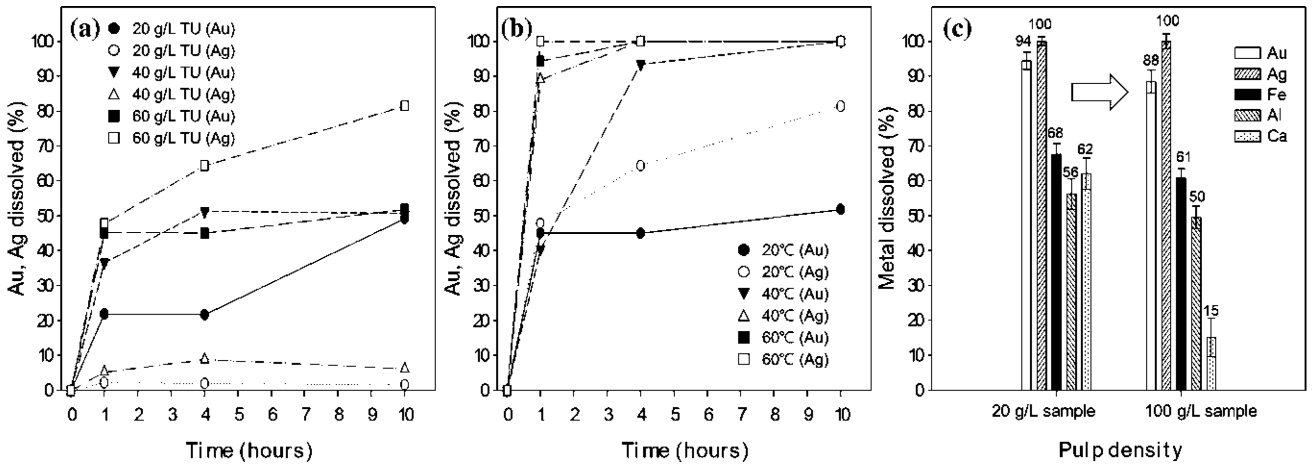

Fig. 1. Effect of various leaching conditions on recovery of Au and Ag: (a) thiourea concentration, (b) temperature, and (c) pulp density.

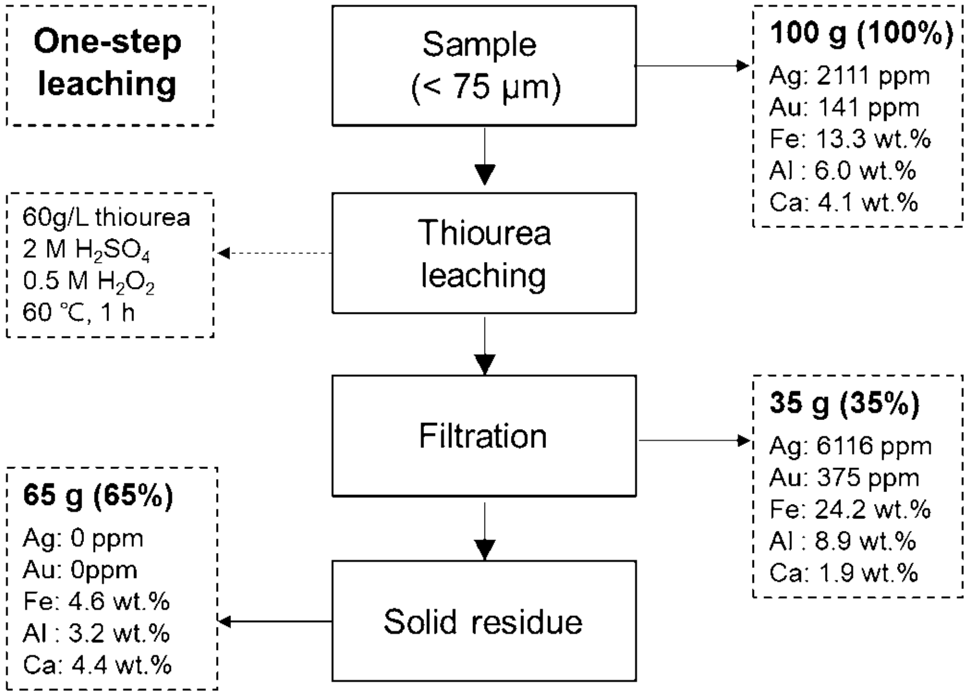

Fig. 2. Mass balance for one-step process for recovery of Au and Ag.

$Fe_2(SO_4)_3$ in thiourea leaching for effective recovery of Au.[11,15] However, it appears to have two disadvantages: consumption of an excessive amount of thiourea due to formation of iron sulfate–thiourea complex and accumulation of impurities which would require a much more expensive purification step.[16] Therefore, in this study, H_2O_2 was used as oxidizing agent without addition of $Fe_2(SO_4)_3$ to avoid such accumulation of impurities.

Figure 1 shows the effect of various leaching conditions on the recoveries of Au and Ag. The effect of thiourea concentration and time on the recoveries of Au and Ag is shown in Fig. 1a. Experiments were conducted at 20°C in 2 M H_2O_4, 0.5 M H_2O_2 solutions with pulp density of 20 g/L. The leaching efficiency for Au and Ag increased with increasing thiourea concentration from 20 g/L to 60 g/L. In particular, the highest Au and Ag leaching efficiency was obtained at thiourea concentration of 60 g/L. The overall reaction (Eqs. 1 and 2) can be expressed as:[17]

$$\begin{aligned} 2\mathrm{Au} + 2\mathrm{CS(NH_2)_2} + (\mathrm{NH_2(NH)CS})_2 \\ + 2\mathrm{H}^+ = 2\mathrm{Au}\left[\mathrm{CN(NH_2)_2}\right]_2^+ \end{aligned} \tag{1}$$

$$\begin{aligned} 2\mathrm{Ag} + 4\mathrm{CS(NH_2)_2} + (\mathrm{NH_2(NH)CS})_2 \\ + 2\mathrm{H}^+ = 2\mathrm{Ag}\left[\mathrm{CS(NH_2)_2}\right]_3^+. \end{aligned} \tag{2}$$

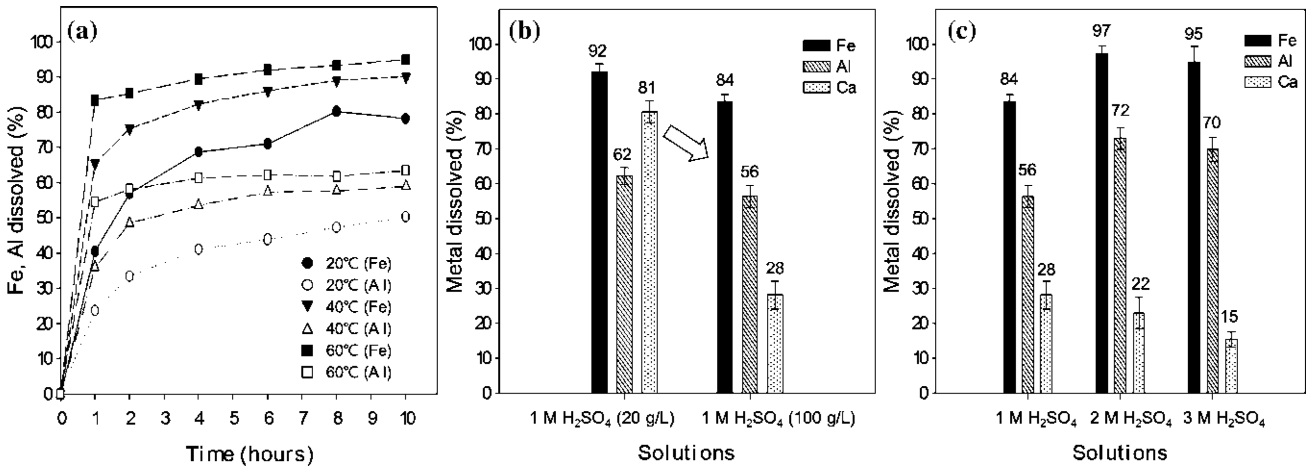

Fig. 3. Effect of various leaching conditions for recovery of Fe and Al: (a) temperature, (b) pulp density, and (c) H_2SO_4 concentration.

This means that the dissolution of Au and Ag is highly dependent on the concentration of thiourea and formamidine disulfide. Thiourea concentration of 60 g/L was selected as the optimum condition for Au and Ag dissolution. Other researchers have also studied the concentration of thiourea that provided the optimum Au efficiency under their experimental conditions.[11,16,17]

Figure 1b shows the effect of temperature and time on the Au and Ag leaching (using thiourea concentration of 60 g/L). The leaching efficiency of Au increased significantly with increasing temperature from 40°C to 60°C for 1 h. The Au and Ag leaching efficiency reached or exceeded 94% after 1 h at 60°C. Therefore, the leaching condition was set at 60°C for 1 h. Figure 1c presents the effect of the pulp density on the Au and Ag leaching efficiency. The pulp density was changed from 20 g/L to 100 g/L, while the other conditions were fixed (60 g/L thiourea concentration, 2 M H_2SO_4, 0.5 M H_2O_2, 60°C, and 1 h). As shown in Fig. 1c, the leaching efficiency of Au and Ag did not change significantly. Although there was a slight decrease in the Au leaching efficiency, the loss was less than 10% because it was present at very low (ppm) levels.

On the basis of the above results, a one-step process for Au and Ag recovery can be proposed, as shown schematically in Fig. 2 with experimental conditions of 2 M H_2O_4, 60 g/L thiourea, and 0.5 M H_2O_2 at 60°C for 1 h. Approximately 35 g of material was leached from the initial sample of 100 g with residue of 65 g. No Au and Ag components were found in the residue, whose metal content was 4.6 wt.% Fe, 3.2 wt.% Al, and 4.4 wt.% Ca. The concentrations of Au and Ag in the leachate were 375 ppm and 6116 ppm, revealing 88–90% Au and 95–100% Ag leaching efficiency. However, about 24.2 wt.% Fe was also dissolved after this one-step leaching process. Such metal ions may act as impurities in Au and Ag extraction processes.

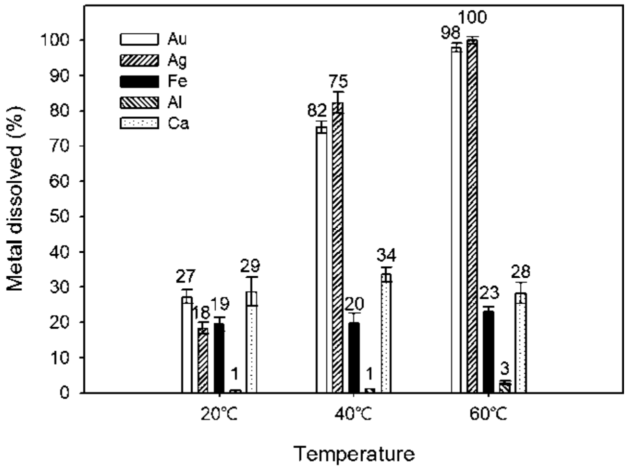

Fig. 4. Effect of temperature on second-stage leaching process: (a) 20°C, (b) 40°C, and (b) 60°C (experimental conditions: 60 g/L thiourea, 2 M H_2O_4, 0.5 M H_2O_2, pulp density 65 g/L, 4 h).

Two-Step Leaching Process for Recovery of Au and Ag

A two-step process was introduced to improve the leaching efficiency and purity of Au and Ag. In the first leaching process, base metals are dissolved in addition to Au and Ag, then the residues of Au and Ag can be accumulated into the solid–liquid separation filter. After that, Au and Ag can be dissolved through a second leaching process.

Figure 3 shows the effect of various leaching conditions for recovery of base metals in the first leaching process. As shown in Fig. 3a, Fe and Al were dissolved up to a maximum of 95% and 63% at 60°C, respectively. Figure 3b and c presents the effects of pulp density and H_2SO_4 concentration during the first leaching process. As shown in Fig. 3b, the leaching efficiency of Fe, Al, and Ca decreased with increasing pulp density from 20 g/l to 100 g/L. In consideration of the increased pulp

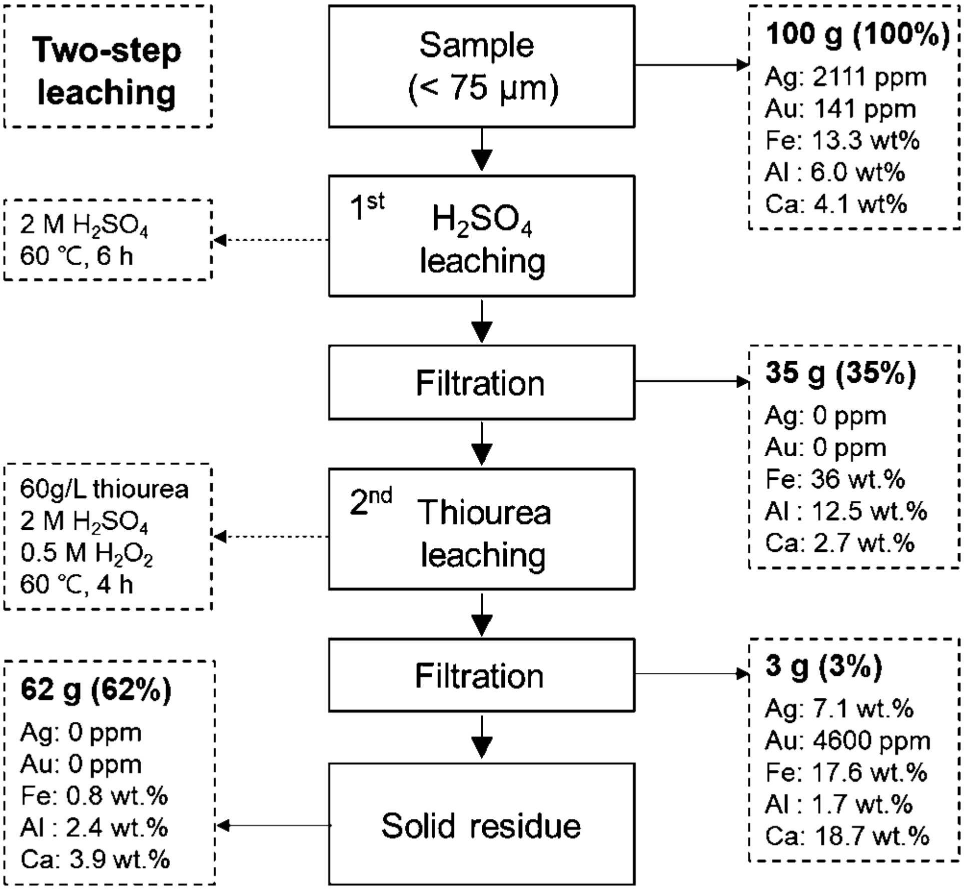

Fig. 5. Mass balance for two-step process for recovery of Au and Ag.

density, the H_2SO_4 concentration was changed from 1 M to 3 M to confirm the leaching efficiency. As shown in Fig. 3c, compared with 2 M and 3 M H_2SO_4 solutions, the leaching efficiency of 2 M H_2SO_4 was slightly higher.

The second leaching experiment was performed using the residue from the first leaching process. Thiourea was also used as a second reagent. Figure 4 shows the effect of temperature on the second leaching process, revealing that 98% Au and 100% Ag leaching efficiency were obtained after 4 h at 60°C. Based on these results, a continuous two-step leaching process for recovery of Au and Ag can be proposed. The mass balance was established for the two-step leaching process. As shown in Fig. 5, approximately 35 g of material was leached in the first process from the initial sample of 100 g with residue of 65 g. The Fe dissolution efficiency was approximately 97%. After that, 3 g of material was obtained from the second leaching process from the first leaching residue of 65 g. The concentrations of Au and Ag in the second leachate were 4600 ppm and 7.1 wt.%. The final dissolution efficiency was 95–98% for Au and 100% for Ag; That is, it is possible to selectively separate each metal through the two-step process, and finally, Au and Ag could be effectively recovered. Depending on the composition of the initial material, the one- or two-step process could be selected. However, it is necessary to analyze the economics of each process according to the initial composition (Au, Ag, and impurities) to determine which process would be more effective.

CONCLUSION

We investigated recovery of Au and Ag from secondary products generated in e-waste processing using thiourea leaching. Thiourea leaching was carried out under various leaching conditions, obtaining Au and Ag leaching efficiencies of about 90% and 100% using one-step thiourea leaching. Using a two-step process, Au and Ag leaching efficiencies of about 98% and 100%, respectively, were obtained. The purity and leaching efficiency of Au and Ag were higher when using the two-stage process compared with the one-stage process. Although this process was investigated for recovery of Au and Ag from e-waste flue dust, it may also be applicable for recovery of secondary metals including Au and Ag generated in other processes (smelting, swarf materials, etc.).

ACKNOWLEDGEMENTS

The authors would like to thank the members of the NSF I/UCRC on Resource Recovery and Recycling (CR^3) and the National Science Foundation for their support of this work.

REFERENCES

1. B.H. Robinson, *Sci. Total Environ.* 408, 183 (2009).
2. R. Widmer, H. Oswald-Krapf, D. Sinha-Khetriwal, M. Schnellmann, and H. Böni, *Environ. Impact Assess. Rev.* 25, 436 (2005).
3. A. Tuncuk, V. Stazi, A. Akcil, E.Y. Yazici, and H. Deveci, *Miner. Eng.* 25, 28 (2012).
4. U. Jadhav and H. Hocheng, *Sci. Rep.* 5, 14574 (2015).
5. A. Kumari, M.K. Jha, and R.P. Singh, *Hydrometallurgy* 165, 97 (2016).
6. Y. Xiao, Y. Yang, J. van den Berg, J. Sietsma, H. Agterhuis, G. Visser, and D. Bol, *Hydrometallurgy* 140, 128 (2013).
7. I. Birloaga, V. Coman, B. Kopacek, and F. Vegliò, *Waste Manag* 34, 2581 (2014).
8. S. Syed, *Hydrometallurgy* 115–116, 30 (2012).
9. G. Hilson and A.J. Monhemius, *J. Cleaner Prod.* 14, 1158 (2006).
10. J. Cui and L. Zhang, *J. Hazard. Mater.* 158, 228 (2008).
11. S. Ubaldini, P. Fornari, R. Massidda, and C. Abbruzzese, *Hydrometallurgy* 48, 113 (1998).
12. M. Vítková, V. Ettler, J. Hyks, T. Astrup, and B. Kříbek, *Appl. Geochem.* 26, S263 (2011).
13. A.N. Banza, E. Gock, and K. Kongolo, *Hydrometallurgy* 67, 63 (2002).
14. A.A. Verbeek and M.C. Mitchell, A. and M. Ure. *Anal. Chim. Acta* 135, 215 (1982).
15. J. Li and J.D. Miller, *Miner. Process. Extr. Metall. Rev.* 27, 177 (2006).
16. R. Ranjbar, M. Naderi, and A. Ghazitabar, *J. Adv. Mater. Process.* 5, 22 (2017).
17. Z. Fang and M. Muhammed, *Miner. Process. Extr. Metall. Rev.* 11, 39 (1992).