Article

Verification of Possibility of Molten Steels Decopperization with ZnAl_2O_4

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Abstract: In the previous research works, ZnAl_2O_4 material was considered as one of the solutions for the decopperization process of molten steels; up to 33% of decopperization efficiency was reported by utilising the ZnAl_2O_4 filter. In order to verify the decopperization possibility of ZnAl_2O_4 materials, iron-based alloys with various copper and carbon contents were interacted with ZnAl_2O_4 substrates in a heating microscope under an argon gas atmosphere at 1600 °C. Fe-Cu alloys were found to react with the ZnAl_2O_4 substrate during the interaction process, and a reaction layer with a complex composition around the alloy droplet was formed; however, Cu was not detected in the reaction layer. Cu was later found infiltrated inside of the ZnAl_2O_4 substrates. Furthermore, the Cu-Zn compounds were detected when the copper content in Fe-Cu alloys was 10 wt% Cu. After interaction experiments, copper was decreased in all cases. Thereby, the copper evaporation and infiltration into the ZnAl_2O_4 substrate were considered as the reasons for copper loss. Moreover, oxygen dissolved in melt was found to have a great effect on the copper evaporation process.

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1. Introduction

After centuries of industry development, steel scrap's stock has become a very prospective raw material resource for steel reproduction. Steel scrap is a cheap but abundant raw material with a high energy content. Every ton of recycled steel scrap saves 1134 kg of iron ore, 635 kg of coal, and 54 kg of lime [1]. However, this new material supplier requires more advanced recycling technology and treatment due to the residual elements contained in the steel scraps.

Copper, as a common tramp element in steel scrap, strongly prevents the effective use of steel scrap, i.e., during the heat treatment process, liquid copper forms and penetrates the grain boundaries, causing cracking [2,3]. As reported in the literature [2], the hot shortness is exhibited when the copper concentration is greater than 0.2 wt%. Copper dissolved in steel melts could not be oxidized in the presence of iron due to its lower affinity for oxygen than iron. Through a common pyrometallurgical method, copper could not be removed from molten steel. In order to apply steel scrap, dilution with virgin pig iron or direct reduced iron (DRI) became the industry solution.

Daehn et al. [4] reported the huge negative influence of copper in constraining future global steel recycling. A variety of methods during the last decades for the removal of copper from steel scrap were suggested based on the unique properties of copper, including that copper has a good affinity to sulfur, a high evaporation rate at high temperatures, and forms volatile gas species with Cl. Thereafter, a series of decopperization methods were reported: (1) treatment by reaction with sulfur-containing slag [5–8]; (2) vacuum distillation [2,9–12]; (3) treatment by reaction with chlorine-containing slag [13]; (4) filtration [2]. More decopperization methods and investigations have been reported and summarized in reviews

by Sandig et al. [14] and Daehn et al. [15]. Besides the above-mentioned methods, a reactive filtration method was reported in earlier literature [16–18]. Wieliczko et al. [16] filtrated copper-containing liquid alloy by applying an Al- and Zn-based ceramic spinel (ZnAl_2O_4); 30–33% copper was removed. Moreover, a 70% of decopperization rate was achieved by blowing fine-grain ZnAl_2O_4 spinel powder into the steel under laboratory conditions. Li et al. [17] stated that intermetallic Cu-Zn compound would be formed by adding Al_2O_3 -ZnO-C materials in liquid Fe-Cu alloy. Namely, the carbon could reduce ZnO (as shown in Equation (1)), then the released Zn would react with Cu and forming Cu-Zn compound. Later, the formed intermetallic Cu-Zn compound would deposit on the surface of Al_2O_3 . Through this process, copper could be successfully removed from the liquid Fe-Cu alloys. The proposed mechanism is illustrated in Figure 1. However, these researchers did not present the in-detail morphology of the Cu-Zn compound formation on Al_2O_3 ceramic with corresponded chemical analysis. Furthermore, the formation of intermetallic compound Cu-Zn was also stated during the welding process between Zn-coated steel and Cu electrodes by Kim et al. [19].

Figure 1. The schematic illustration of proposed filtration mechanism by ZnAl_2O_4 as filter materials.

The unclarified copper-filtration possibility of ZnAl_2O_4 filter and the urgency of finding an efficient decopperization method led the present work aim to verify the possibility of ZnAl_2O_4 as a prospective solution for decopperization. Therefore, in the present work, various contents of copper-/carbon-bearing iron were interacted with ZnAl_2O_4 substrate. For the comparison, pure alumina was also interacted with alloy samples.

2. Materials and Methods

2.1. ZnAl_2O_4 Substrates' Preparation

To prepare the used ZnAl_2O_4 -substrates, pure ZnO (90/RS Carl Jäger, Hilgert, Germany) and Al_2O_3 (Martoxid[®]MR70, Martinswerk, Bergheim, Germany) were used. The raw materials were mixed in a molar ratio of 48 mol% Al_2O_3 and 52 mol% ZnO. A water-based slurry containing the oxides as well as 0.4 wt% Displex[®] A40 (CIBA, Basel, Switzerland) as a wetting agent and 0.2 wt% Optapix[®] AC170 (Zschimmer&Schwarz, Lahnstein, Germany) as a pressing agent were mixed with 25 wt% distilled water (related to dry mass of oxides) in a PET container with alumina balls. The container was rotated for 12 h to homogenize the slurry. After that, the mixture was dried at 110 °C to less than 3% water. The dried raw material was crushed and sieved to less than <1 mm maximum grain size. The prepared granules were now 120 MPa uniaxial pressed to substrates with a diameter of 50 mm and a thickness of 5 mm and sintered in an electric-heated furnace under an oxidizing atmosphere at 1600 °C with a heating rate of 2 K/min and a dwell time

of 5 h. After the sintering step, the substrates were grinded and polished on one side to ensure a flat surface for the wetting experiments. XRD (in Figure 2) investigations show the conversion of 96.6 wt% ZnAl_2O_4 and 3.4 wt% ZnO reaction product.

Figure 2. X-ray diffraction profile collected from prepared ZnAl_2O_4 substrates.

2.2. Fe-Cu Alloys' Preparation and Experimental Setup

A cold crucible induction melter KIT (CCIM KIT) (LINN High Therm GmbH, Eschenfelden, Germany) was applied to produce Fe-Cu alloys. The in-detailed description about CCIM is reported elsewhere [20]. Armco iron with the composition as shown in Table 1, pure copper (99.999%), and graphite were used as primary materials for the sample preparation. The prepared Fe-Cu alloys are listed in Table 2. The Fe-Cu alloy samples were prepared into a cylindrical form with a height of 8 mm and diameter of 7.5 mm, then etched with HCl and H_2O ($\text{HCl}/\text{H}_2\text{O} = 1:1$) mixed solution.

Table 1. Chemical compositions of Armco-iron (ppm).

Armco Iron	Fe (wt%)	C	Mn	Si	Al	O
	99.8	40	30	262	11	92

The experimental interaction was conducted in a heating microscope under argon with a flow rate of 0.3 L/min (2–3 ppm oxygen) at 1600 °C. Both the heating and cooling rate were kept at 40 K/min. The interaction process was monitored by a CCD camera (IMAGINGSOURCE GmbH, Bremen, Germany). A simplified schematic illustration of the experimental setup is shown in Figure 3. An in-detail description was presented in the previous publication [21]. The conducted experiments are summarized in Table 2.

Table 2. The conducted interaction experiments.

Fe-Cu (wt%)	ZnAl_2O_4	Al_2O_3
0.5% Cu, 40 ppm C	90 min	90 min
0.5% Cu, 0.5% C	90 min	90 min
1% Cu, 40 ppm C	90 min	90 min
1% Cu, 0.5% C	90 min	90 min
10% Cu, 40 ppm C	90 min	-

Figure 3. Schematic view of interaction experimental procedure.

The general chemical composition of iron alloys was analyzed by the spark spectrometer Foundry-Master UV (Oxford Instruments, Abingdon, England). Moreover, Bruker G4 Ikarus and Bruker G8 Galileo combustion analyzers were applied to estimate the O, C, and S contents. After the interaction experiments, metal droplet and ZnAl_2O_4 substrates were embedded into epoxy resin and perpendicularly cut for cross-sectional analysis. Scanning electron microscopy (SEM) in combination with energy-dispersive X-ray spectroscopy (EDX) was used for morphology and chemical determination (Ultra55, Zeiss NTS GmbH, Heidelberg, Germany).

3. Results and Discussion

3.1. Experimental Observation

A melting mechanism of Fe-Cu alloys on ZnAl_2O_4 substrate is illustrated in Figure 4a. As shown in Figure 4a, Fe-Cu alloys start to melt when the temperature is high enough (melting temperature of iron 1538 °C). Later, a symmetrical liquid droplet is formed. With a longer interaction period, the Fe-Cu alloys liquid spread on the ZnAl_2O_4 substrate. Moreover, during all the interaction experiments, the formation of gas bubbles inside the molten Fe-Cu alloys was observed; with the addition of 0.5 wt% C, the gas formation was much heavier than 40 ppm C.

Figure 4. Melting mechanism of steel. (a) Schematic illustration of Fe-Cu sample melting mechanism on the ZnAl_2O_4 substrate. (b) Image of melted Fe-Cu on ZnAl_2O_4 substrate. (c) Image of melted Fe-Cu on Al_2O_3 substrate.

Figure 4b indicates an image of liquid Fe-Cu (1 wt% Cu) alloys spread on the ZnAl_2O_4 substrate. Furthermore, after interaction with the ZnAl_2O_4 substrate, a reactive layer and plenty of powder were found in the experimental chamber; according to the chemical analysis, this powder consisted of ZnO. It indicates that the ZnO in the ZnAl_2O_4 substrate was reduced by the carbon contained in the Fe-Cu alloys, then re-oxidized by the oxygen contained in the protective gas. On the other hand, a perfect symmetrical Fe-Cu alloy liquid droplet was presented on the Al_2O_3 substrate, as shown in Figure 4c. No reaction was observed.

3.2. Interfacial and Cross Sectional Analysis

Figure 5a shows an image of Fe-1% Cu alloy interacted with ZnAl_2O_4 substrate; a reaction layer was formed around iron sample. According to the SEM/EDX analysis, the reaction layer consists of complex elements including O, Al, Fe, Zn, Mn, and Si without Cu. (see Figure 5b,d)). Elements such as Si, Mn, and Fe are transferred from the side of the iron sample. At the cross section (see Figure 5c), only some Fe was detected.

Figure 5. (a) Image of Fe-1% Cu interaction with ZnAl_2O_4 substrate. (b) morphology of reaction layer. (c) morphology of cross section of substrate. (d) EDX result.

Figure 6a indicates the cross section between Fe-1% Cu-0.5% C alloy and ZnAl_2O_4 substrate. The cross section was divided into four different subareas; the copper content was EDX measured at each subarea; the measured copper content is depicted in Figure 6c. The copper content decreases from the ZnAl_2O_4 substrate interface (Figure 6a, subarea 4) to inside of the substrate. Figure 6b indicates the Fe-Cu alloy interaction area, according to the measured point 1 and 2 (Figure 6b), the detected ratio of Cu and Fe in ZnAl_2O_4 substrate is similar to with Fe-1% Cu alloy. It indicates that Cu was infiltrated into the ZnAl_2O_4 substrate along with liquid Fe-Cu alloy; the formation of intermetallic compound Cu and Zn was not detected.

Figure 6. (a) Cross section of Fe-1% Cu-0.5% C alloy interaction with ZnAl_2O_4 substrate; cross section was separated into 4 subareas; subarea 4 indicates the iron contacted area. (b) morphology of reaction layer. (c) copper contents at different subareas (1–4) as indicated in figure (a). (d) EDX values on point 1 and point 2.

After the interaction between iron alloy with 10 wt% Cu and ZnAl_2O_4 substrate, metallic Cu was detected on the bottom of the newly formed reactive layer as shown in Figure 7a. Figure 7b is the cross-section area between alloy and substrate, it shows that the compounds with bright colour were scattered in this area. EDX analysis revealed that point 3 (86.84 wt% Cu) is pure copper, which is transferred from the Fe-10% Cu sample side. Furthermore, point 4 consists mostly of Al and Fe. Finally, the element's ratio (Cu/Zn = 0.6) at point 5 indicates that it is a Cu_5Zn_8 compound.

Figure 7. (a) Image of Fe-10% Cu alloy bottom after interacting with ZnAl_2O_4 substrate. (b) morphology of cross section between Fe-10% Cu alloy and ZnAl_2O_4 substrate. (c) morphology of cross section. (d) EDX values on points 3–5.

Fe-Cu alloy is known as an alloy with a metastable miscibility gap. During the solidification process, if a single-phase liquid is undercooled into the metastable miscibility gap, it will divide into two liquids, iron and copper [22]. According to Brillo and Egry [23], the energy of mixing ΔG is strongly positive for Fe-Cu. Consequently, Fe-Cu does not form a homogeneous solution at all temperatures and compositions. Since copper has a greater density than iron [24], it could accumulate at the bottom of the alloys.

3.3. The Composition of Fe-Cu Alloys

The measured chemical compositions of Fe-Cu alloys after the interaction are listed in Table 3. The copper content was found to be decreased in all cases. For the Al_2O_3 substrate cases, the copper losses at various cases were close to each other; the copper loss was considered as mainly contributing to the copper evaporation. Moreover, the oxygen content was slightly decreased for Al_2O_3 substrate cases. In the heating microscope, a graphite tube is installed for the heating process; it could react with the oxygen contained in the protective gas forming CO gas. Hence, the formed carbon monoxide (CO) in the experimental atmosphere might decrease a fraction of oxygen in the liquid samples. Furthermore, when liquid Fe-Cu alloy interacts with ZnAl_2O_4 substrates, more copper was found vanished with the addition of 0.5% carbon. For ZnAl_2O_4 substrates, copper evaporation into the atmosphere and transfer into the ZnAl_2O_4 substrates were the reasons for the copper loss. Thereby, with an addition of carbon content (0.5 wt% C) in the Fe-Cu alloys, more ZnO was reduced into Zn and O; it increased the porosity of the ZnAl_2O_4 substrates. Furthermore, due to the positive mixing energy ΔG for molten Fe-Cu and high density of copper [23], more copper would accumulate at the liquid sample's bottom. Therefore, more copper would have infiltrated into the ZnAl_2O_4 substrates along with liquid Fe-Cu samples.

Table 3. Chemical composition of Fe-Cu samples after experiments (ppm).

wt%	C	Si	Mn	Al	O	Cu Wt%	Cu Loss (%)
0.5% Cu Al_2O_3	40	58	16	36	72	0.382	23.4
0.5% Cu ZnAl_2O_4	15	138	13	41	423	0.411	17.6
1% Cu Al_2O_3	40	91	15	55	80	0.718	28.2
1% Cu ZnAl_2O_4	13	77	13	28	559	0.908	9.2
0.5% C 0.5% Cu Al_2O_3	0.516 wt%	50	27	38	51	0.35	25.0
0.5% C 0.5% Cu ZnAl_2O_4	14	50	13	38	252	0.321	31.3
0.5% C 1% Cu Al_2O_3	0.457 wt%	50	15	45	62	0.757	24.3
0.5% C 1% Cu ZnAl_2O_4	18	66	13	46	301	0.722	27.8

In the meantime, the reduction of ZnO in ZnAl_2O_4 substrates supplied the oxygen into Fe-Cu alloys; consequently, the oxygen content after interaction with ZnAl_2O_4 substrates was increased. Besides this, aluminium was found to slightly dissolve into the iron sample and after interaction with Al_2O_3 and ZnAl_2O_4 substrates. According to the previous literature [21,25], under present low-oxygen partial pressure and high temperature, Al_2O_3 would dissolve into the liquid iron. The carbon content was strongly decreased after interacting with ZnAl_2O_4 substrates. However, the carbon content after making contact with the Al_2O_3 substrates kept the same.

3.4. Copper Evaporation Mechanism

In the present investigation, copper was mainly decreased due to its high evaporation rate. According to the literature related to the copper evaporation [10,26–29], the copper evaporation process from liquid iron can be divided into three main stages: (1) copper transfer from the bulk of the liquid phase to the interface; (2) copper evaporation from the liquid metal surface; (3) transfer of the copper vapours from the interface to the core of the gaseous phase, as illustrated in Figure 8.

Fischer et al. [30] stated that the apparent evaporation rate constant k_{Cu} can be expressed by Equation (2). As shown in Equation (2), k_{Cu}^L is liquid phase mass transfer

coefficient ($\text{m}\cdot\text{s}^{-1}$), k_{Cu}^e is the free evaporation rate constant of Cu ($\text{m}\cdot\text{s}^{-1}$), and k_{Cu}^G is the gas phase mass transfer coefficient ($\text{m}\cdot\text{s}^{-1}$).

$$k_{\text{Cu}} = \frac{1}{\frac{1}{k_{\text{Cu}}^L} + \frac{1}{k_{\text{Cu}}^e} + \frac{1}{k_{\text{Cu}}^G}} \quad (2)$$

Figure 8. The mechanism of copper evaporation from liquid Fe-Cu alloy. (a) Copper transfer from the bulk of the liquid phase to the interface. (b) copper evaporation from the liquid metal surface. (c) transfer of the copper vapors from the interface to the core of the gaseous phase.

3.5. Effect of Oxygen on Copper Evaporation

Oxygen is known as a surface-active element; it accumulates on the liquid Fe-Cu alloy surface and blocks the available sites for metal–gas reactions. Consequently, oxygen prevented the copper evaporation to atmosphere, as illustrated in Figure 9. Furthermore, a few ppm of oxygen can significantly reduce the surface tension value [31]. Thereby, its effect on the free evaporation rate constant of copper from liquid iron can be expressed by assuming Langmuir’s ideal adsorption isotherm [32,33].

$$k_{\text{Cu}}^e = k_{\text{Cu}}^{e0}(1 - T_O) \quad (3)$$

where k_{Cu}^e is the free evaporation rate constant of Cu on the surface of liquid iron ($\text{m}\cdot\text{s}^{-1}$), k_{Cu}^{e0} is the free evaporation rate constant of Cu on the surface of oxygen free liquid iron ($\text{m}\cdot\text{s}^{-1}$) and T_O is the degree of surface coverage by absorbed oxygen.

$$K_O^{\text{Cu}} \cdot a_O = \frac{T_O}{(1 - T_O)} \quad (4)$$

where K_O^{Cu} is the adsorption equilibrium constant of oxygen on the surface of liquid iron and a_O is the activity of oxygen in liquid iron.

$$k_{Cu}^e = \frac{k_{Cu}^{eo}}{(1 + K_O^{Cu} \cdot a_O)} \quad (5)$$

The value of K_O^{Cu} was reported as 110 in the Equation (6) by Lee [34].

$$Y_{Fe-O} = 1.890 - 0.299 \ln(1 + 110 a_O) \quad (6)$$

Therefore, high oxygen content greatly prevented the copper evaporation in the Fe-Cu alloys. Carbon addition would decrease the oxygen content in the melts and enhance the copper evaporation.

Moreover, oxygen reduces the activity coefficient of copper γ_{Cu} (as shown in (7)) in the liquid iron, due to the negative interaction coefficient between copper and oxygen, $e_{Cu}^O = -0.05$ at 1600 °C [35].

$$\log \gamma_{Cu} = \sum_i e_{Cu}^i [\text{mass}\% i] = e_{Cu}^i \cdot [\text{mass}\% i] + e_{Cu}^O \cdot [\text{mass}\% O] \quad (7)$$

where i is the elements in the Fe-Cu alloy and e_{Cu}^i is interaction coefficient of Cu in the liquid iron.

Figure 9. Illustration of oxygen blocks the free sites for copper evaporation on liquid Fe-Cu alloy surface.

4. Conclusions

Both $ZnAl_2O_4$ and Al_2O_3 substrates have interacted with liquid Fe-Cu alloys containing carbon to verify the decopperization possibility of $ZnAl_2O_4$ materials. After experiments, copper was found to decrease with both $ZnAl_2O_4$ and Al_2O_3 substrates. The copper evaporation and its infiltration along with liquid Fe-Cu alloys into the $ZnAl_2O_4$ substrate were the explanations for the copper loss. For the Fe-Cu (0.5–1.0 wt% Cu) alloys, no metallic Cu and Zn compounds were detected with $ZnAl_2O_4$ substrates. The intermetallic compound Cu_5Zn_8 was only detected with Fe-Cu (10 wt% Cu) alloy. According to the obtained experimental results, it can be concluded that the decopperization of liquid steels with $ZnAl_2O_4$ filter is implausible.

Besides this, the oxygen contents after interacting with $ZnAl_2O_4$ substrates were strongly increased with the decompose of ZnO. The oxygen dissolved into the liquid Fe-Cu alloys noticeably affected the copper evaporation, which led to a lower copper loss. Based on the experimental results, $ZnAl_2O_4$ materials showed a higher decopperization efficiency when the Fe-Cu alloys contained more carbon. However, this result was caused by the infiltration of Fe-Cu alloys into the $ZnAl_2O_4$ substrate with enhanced porosity.

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