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RECYCLING AND UTILIZATION OF SPENT MOLYBDENUM DISILICIDE: PREPARATION OF COATING AND METAL RECOVERY VIA SYNERGISTIC SMELTING

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Abstract

Molybdenum disilicide ($MoSi_2$) heating elements are widely used in the industrial and laboratory high-temperature heating field. Based on the excellent oxidation resistance of $MoSi_2$, solid waste from spent heating elements was used as raw material to fabricate silicide-based anti-oxidation coatings on refractory metals (Mo, Nb, etc.). After oxidation at 1500 °C for 40 hours, the coating exhibited a minimal weight gain of 2.78 mg/cm^2, and the surface formed a crack-free, continuous SiO_2 oxide film. The coating demonstrated dense morphology, controllable thickness, uniform composition, and strong interfacial bonding.

Given the high molybdenum content in spent molybdenum disilicide and the elevated iron content in metallurgical iron-containing slags, the two solid wastes were subjected to synergistic reduction smelting. Through high-temperature pyrolysis of $MoSi^2$, silicon and iron reduction, in situ generation of molybdenum and iron, the key metal molybdenum in retired silicon molybdenum was selectively recovered, and molybdenum alloy was synchronously prepared in situ. The recovery efficiencies reached 99.97 % for molybdenum and 85.49 % for iron, achieving synergistic high-value utilization of high-grade metals from multi-component solid wastes.

Keywords: *Spent molybdenum disilicide; Coating; Molybdenum iron recovery; Comprehensive recovery*

1. INTRODUCTION

$MoSi_2$ is a widely applied Dalton-type intermetallic compound with excellent high-temperature oxidation resistance [1], commonly used as a raw material for high-temperature electric furnace heating elements [2]. However, with the increasing demand for $MoSi_2$ heating elements, large quantities of spent $MoSi_2$ components are discarded, posing significant environmental and resource challenges [3]. Due to its oxidation-resistant properties, spent $MoSi_2$ can serve as a precursor for high-temperature oxidation-resistant coatings [4]. Additionally, its high molybdenum content and the reducibility potential of silicon enable $MoSi_2$ to act as a reductant for recovering valuable metals from iron-rich slags with high oxygen potential. Copper slag, a major byproduct of pyrometallurgical copper production (generating 2.2–3 tons per ton of copper produced) [5], contains 35–45 wt.% Fe and holds significant recycling value. Currently, most copper slag is directly disposed of in slag disposal pits without treatment, causing severe resource waste and environmental hazards. Its efficient processing and recycling have become urgent priorities.

This study employs spark plasma sintering (SPS) to fabricate dense, thickness-controlled $MoSi_2$ coatings on Nb substrates, addressing high-temperature oxidative demands. SiC/$ZrSi_2$ additives modulate thermal expansion mismatch, enhancing high-temperature durability. A synergistic smelting process recovers spent $MoSi_2$ and copper slag: Si acts as a reductant, generating SiO2 slag to optimize dynamics, while in situ MoFe formation improves metal capture. Copper slag

serves as a low-melting flux and Fe source, accelerating $MoSi_2$ decomposition and enabling efficient slag-metal separation. This strategy achieves selective MoFe recovery.

2. EXPERIMENTAL

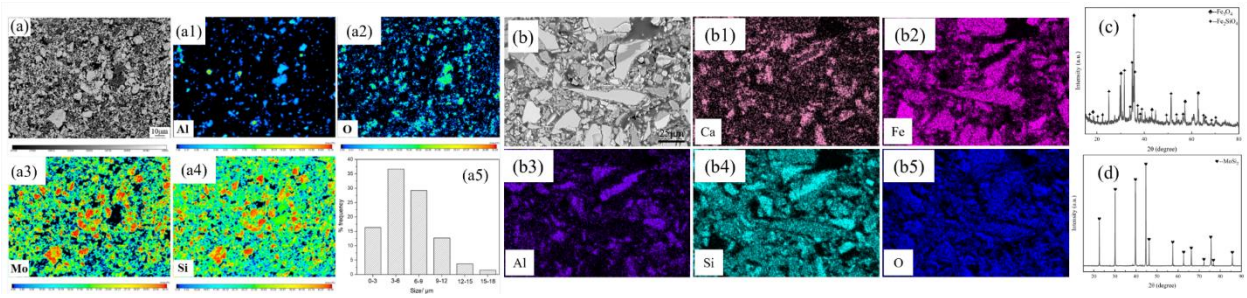

Figure 1. (a) EPMA image of spent $MoSi_2$ powder; (b) SEM image of copper slag powder; (c) XRD results of copper slag; (d) XRD results of spent $MoSi_2$ powder.

The spent $MoSi_2$ powder used in the experiments was derived from Grade 1800 molybdenum disilicide rods, prepared via crushing and ball-milling. It was primarily composed of the $MoSi_2$ phase (confirmed by XRD, Fig. 1d). EPMA mapping (Fig. 1a) revealed Mo, Si, Al, and O elements, minor Mo_5Si_3 phase. The copper slag (from a Chinese enterprise) was depleted slag dominated by fayalite and magnetite phases (Fig. 1c). SEM-EDS mapping (Fig. 1b) showed fayalite as regular gray blocks, magnetite as bright white regions, and interspersed dark-phase gangue. Coating sintering was performed at 1500 ℃ using an SPS system (Labox-125, Sinter Land Inc., Japan). Synergistic smelting of copper slag and spent $MoSi_2$ was conducted in a tube furnace.

3. RESULTS AND DISCUSSION

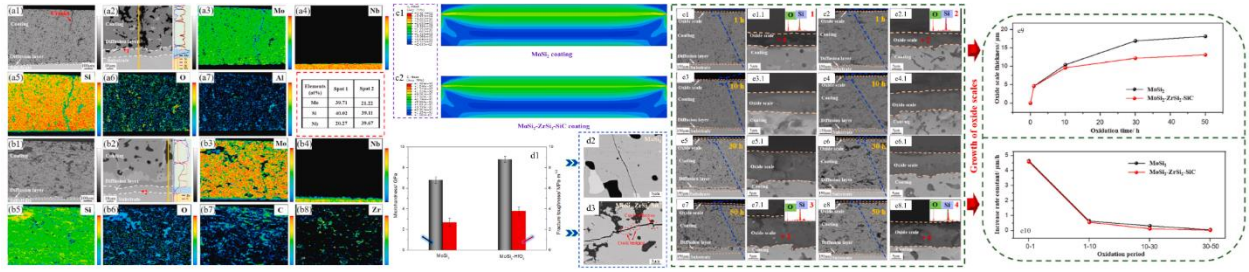

Figure 2. (a) Cross-section BSE micromorphology and WDS analysis of SPSed $MoSi_2$ and (b)$MoSi_2$-$ZrSi_2$-SiC coatings; Stress distribution diagrams of $MoSi_2$ (c1) and $MoSi_2$-$ZrSi_2$-SiC (c2) coatings on Nb substrate after SPS; Microhardness and fracture toughness of SPSed $MoSi_2$ and $MoSi_2$-$ZrSi_2$-SiC coatings (d1); indentation morphologies of the crack propagation path of $MoSi_2$ (d2)and $MoSi_2$-$ZrSi_2$-SiC (d3) coatings; (e) Cross-section BSE micromorphology and EDS analysis of XRD patterns of $MoSi_2$ and $MoSi_2$-$ZrSi_2$-SiC coatings after oxidation of 1-50 h at 1500 ℃; Corresponding oxide scale thickness and increase rate constant of $MoSi_2$ and $MoSi_2$-$ZrSi_2$-SiC coatings during oxidation

After high-temperature sintering, the $MoSi_2$ coating exhibited strong adhesion to the substrate (Fig. 2a), with an 11.2 μm $(Nb, Mo)_5Si_3$ diffusion layer formed beneath the coating, enhancing interfacial bonding. However, CTE mismatch induced through-thickness cracks in the MoSi2 coating post-sintering. SiC incorporation mitigated CTE mismatch, improving coating integrity (Fig. 2b). Residual thermal stresses were primarily localized in the $MoSi_2$ coating, but the $MoSi_2$-$ZrSi_2$-SiC composite coating showed a more uniform stress distribution due to optimized CTE compatibility (Fig. 2c). Calculated residual stresses in monolithic $MoSi_2$ (0.5 GPa) exceeded those in the composite coating (0.2 GPa), indicating reduced interfacial thermal stress. This ensured robust bonding, suppressed crack propagation after SPS, and enhanced fracture toughness via

crack deflection, complex propagation paths, and energy absorption (Fig. 2d). SiC particles further increased coating hardness.$ZrSi_2$ addition promoted the formation of high-melting-point $ZrO_2/ZrSiO_4$ skeletons during oxidation, improving oxide scale stability and density (Fig. 2e).

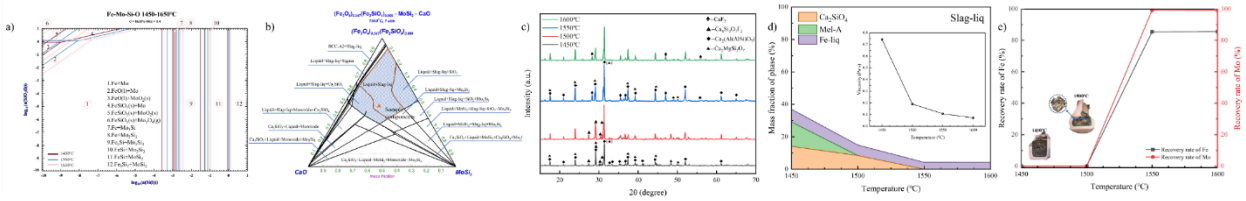

Figure 3. (a) Phase diagram of the Fe-Mo-Si-O system at different temperatures; (b) The ternary phase diagram of the main components of copper slag - $MoSi_2$ - CaO system; (c) XRD results of secondary slag; (d) Phase composition at different temperatures; (e) The influence of temperature on the extraction yields of Mo and Fe

The Fe–Mo–Si–O equilibrium predominance area diagram (Fig. 3a) shows that Fe and Mo can co exist as metallic phases with enrichment. However, Si's reducing capability weakens at elevated t emperatures, causing Mo oxidation loss. Calculations of the $MoSi_2$–copper slag major componen ts–CaO ternary phase diagram (Fig. 3b) indicate that moderate CaO addition expands the coexist ence region of slag and alloy liquids, reduces high-melting-point phases, and optimizes reaction t hermodynamics and processing environments. High-temperature melting experiments (Fig. 3c) re veal dominant slag phases as CaO–SiO_2 glass melt and gehlenite. CaF_2 addition lowers melt visc osity and melting point by acting as a diluent for [SiO_4] networks. Increasing temperature signific antly enhances refractory phase dissolution (Fig. 3d), reduces melt viscosity, and improves reacti on conditions and settling efficiency, achieving Mo and Fe recovery rates of 99.97 % and 85.49 %. However, excessive temperatures induce Mo oxidation loss (Fig. 3e).

4. CONCLUSION

This study employed SPS to fabricate composite coatings on Nb substrates using spent MoSi2 as the primary raw material, with minor additions of SiC and ZrSi2. The coatings exhibited excellent mechanical properties and high-temperature oxidation resistance, demonstrating robust anti-oxidation and oxygen-barrier capabilities during a 50-hour oxidation test at 1500 °C. Leveraging the reducing potential of silicon in spent MoSi2, synergistic smelting of copper slag and spent MoSi2 was conducted to in-situ fabricate ferromolybdenum alloys. Under optimal process conditions, Mo and Fe recovery efficiencies reached 99.97% and 85.49%, respectively. This approach achieved waste-to-waste treatment and cradle-to-cradle life cycle recycling of wastes.

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