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Enhancing Wear Resistance of Co-Cr-Mo-*x*C F75 Implants: The Role of Cooling Rate in Microstructural Evolution

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Abstract

Cobalt (Co)-based metal alloys are widely used in biomaterial applications, particularly for joint replacements, due to their superior wear resistance compared to other metal implant materials like stainless steel and titanium. The wear resistance of as-cast Co-Cr-Mo alloys is influenced by precipitates formed during the alloy's solidification process. To enhance hardness and wear resistance, researchers conducted experiments using heat treatment with varying cooling rates and carbon compositions to examine their effects on microstructure, hardness, and wear resistance. Specimens with carbon compositions of 0.08% and 0.15% were cut into 40 mm × 14 mm × 14 mm pieces and subjected to heat treatment at 1050°C for 6 hours with different cooling rates (DF, UT, and QC specimens). One QC specimen underwent additional aging at 815°C for 6 hours. After preparation, the specimens were machined and tested for wear resistance using the pin-on-disk method, with Co-Cr-Mo pins and alumina disks immersed in Hank's solution. Eluted ions were analyzed using Inductively Coupled Plasma (ICP). The results showed that higher carbon composition increased hardness, but wear resistance did not correlate directly with hardness. The highest hardness value (362.562 HV) was observed in the 0.15% C alloy (QC specimen), while the lowest total ion elution (8.4881 ppm) occurred in the 0.15% C alloy (UT specimen).

Keywords: Co-Cr-Mo; Hardness, Heat treatment; Wear resistance; Pin on disk.

1. Introduction

The world is currently entering an era of an aging population, with individuals aged 60 and above accounting for more than 7% of the global population [1]. In 2024, the elderly population in Indonesia reached 9.92%, or approximately 26.82 million people. Nearly half (48.14%) of Indonesia's elderly population reported physical and psychological health issues, primarily due to degenerative diseases associated with aging [2]. One such condition is osteoarthritis, a chronic joint disorder affecting around 7% of the global population over 500 million people. The World Health Organization (WHO) estimates that by 2025, Indonesia's elderly population will increase by 414% compared to 1990 levels [3].

Co-Cr-Mo alloy, a widely used implant material compliant with ASTM F75 standards, is favored for its excellent mechanical properties, biocompatibility, wear resistance, and corrosion resistance [4]. However, a major challenge arises in high-friction areas like the hip joint, where constant bone contact generates wear debris and metal ion release. These byproducts can lead to local tissue inflammation, metal allergies, DNA damage, and inflammatory cell death [5].

The primary concerns with metal-based hip replacements are wear debris formation and ionic elution, which are closely linked to the microstructure and precipitates of the Co-Cr-Mo alloy [6]. Since the microstructure significantly influences the mechanical and tribological properties of cobalt-based alloys, optimizing it can help reduce wear in hip and knee prostheses [7]. Additionally, precipitates in Co-Cr-Mo alloys play a crucial role in wear resistance [8]. The wear-resistant properties of ASTM F75 Co-Cr-Mo alloy depend on the phase, quantity, size, and distribution of precipitates within the metal matrix [9]. These factors are influenced by heat treatment, as the cooling rate affects carbide precipitate size—with rapid cooling producing a finer, equiaxed microstructure that enhances mechanical properties [10, 11].

Heat treatment involves heating a metal to a specific temperature in a furnace, followed by controlled cooling using a selected medium. This process modifies the microstructure, improving the alloy's properties [12]. To investigate these effects, this study examines how heat treatment and carbon composition in Co-Cr-Mo alloys influence hardness and wear resistance under different cooling rates. Wear resistance testing was conducted using a pin-on-disk method with simulated body fluid to evaluate performance under biologically relevant conditions.

2. Materials and Methods

The study utilized Co-Cr-Mo ingots compliant with ASTM F75 standard, containing carbon compositions of 0.08% and 0.15%. was carried out as cast using VAR with an argon vacuum. The chemical compositions of Co-Cr-Mo ingots are shown in Table 1.

Table 1. Chemical composition of Co-Cr-Mo alloy (wt.%).

Alloy	Co	C	Cr	Mo	Si	Mn	Fe	Ni
0,08C	Bal.	0,08	28	6	0,8	0,8	0,4	0,2
0,15C	Bal.	0,15	28	6	0,8	0,8	0,4	0,2

The ingots were initially cut into specimens measuring 40 mm × 14 mm × 14 mm. Heat treatment was conducted at 1050°C for 6 hours in a furnace, followed by different cooling methods: furnace cooling (slow cooling), air cooling (moderate cooling), and quenching (rapid cooling, with two specimens undergoing this process). One of the quenched specimens subsequently underwent an aging process at 815°C for 6 hours.

Following heat treatment, all specimens were machined into cylindrical shapes with dimensions of 40 mm in length and 5 mm in diameter.
Wear resistance testing was performed under controlled conditions using a load of 1 kgf (166 MPa, based on Hertzian contact stress) with Hank's solution as the simulated body fluid. The tests were conducted at a sliding speed of 16 rpm (25 mm/s) for a duration of 259.2 ks (3 days) for each specimen. Material characterization included hardness measurements using a Vickers hardness tester and microstructural analysis through both Optical Microscopy (OM) and SEM-EDS (Scanning Electron Microscopy-Energy Dispersive X-ray Spectroscopy). Prior to microscopic examination, specimens were prepared by mechanical grinding with emery paper (up to #1200 grit), polishing with alumina paste, and electrolytic etching in a 10% methanol and H_2SO_4 solution at 6 V. Additionally, metal ion concentrations in the filtrate were quantitatively determined using Inductively Coupled Plasma (ICP) analysis.

3. Results and Discussions

3.1 Effects of Heat Treatment and Carbon Content on the Microstructure of Co-Cr-Mo Alloys

The metallographic observations conducted using optical microscopy (OM) on AC (As-cast), DF (Furnace-cooled), UT (Air-cooled), QC(Quenched) and AG (Aged) specimens are presented in Figures 1 and 2. These images reveal the microstructure morphology of the Co-Cr-Mo alloy, showing precipitates distributed throughout the matrix. The microstructural characteristics vary depending on both the heat treatment process and carbon composition.

Figures 1a and 2a demonstrate that the as-cast specimens contain black, blocky-shaped precipitates. According to XRD analysis by Alfirano et al. [13], these precipitates in the 0.08C alloy consist solely of the χ phase, which forms due to the low carbon content during casting. The χ phase, known to be detrimental to manufacturing processes, typically appears in alloys with low carbon and nitrogen content. In contrast, higher carbon compositions promote the formation of M23X6-type carbides as the dominant phase [13]. Figures 1b-e and 2b-e show microstructures with smaller blocky precipitates accompanied by fine lines indicative of martensite formation. Kurosu et al. [14] attribute these features to the $\gamma \rightarrow \varepsilon$ martensitic transformation that occurs during aqueous quenching.

Carbon plays a crucial role in precipitate formation within cobalt-based alloys [15]. In Co-Cr-Mo alloys, precipitates generally fall into two categories: intermetallic compounds and carbonitrides. Narushima et al. demonstrated that carbon content significantly influences both the phase composition and morphological characteristics of these precipitates [16]. Comparative analysis of the 0.08C and 0.15C alloys (Figures 1 and 2) reveals that the higher-carbon specimens contain substantially more precipitates. This difference occurs because carbon acts as a strong carbide-forming element, primarily generating M23C6-type phases [15]. The reduced solubility of precipitates at higher carbon content leads to increased precipitation, as confirmed by quantitative image analysis using ImageJ software, see Figure 3. The data clearly show that precipitate content increases proportionally with carbon composition, as carbon reacts with metallic elements to form additional precipitates [13].

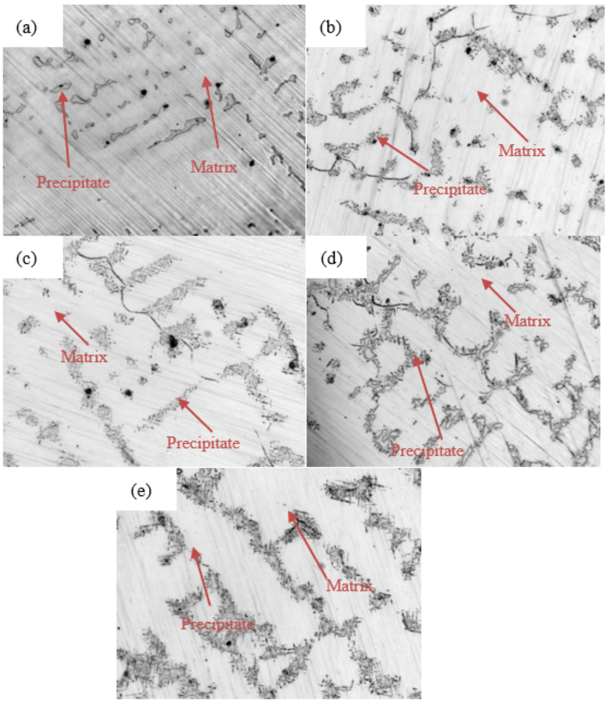

Figure 1. Microstructure using an optical microscope magnification of 200x for 0,08C alloy (a) AC, (b) DF, (c) UT, (d) QC, (e) AG

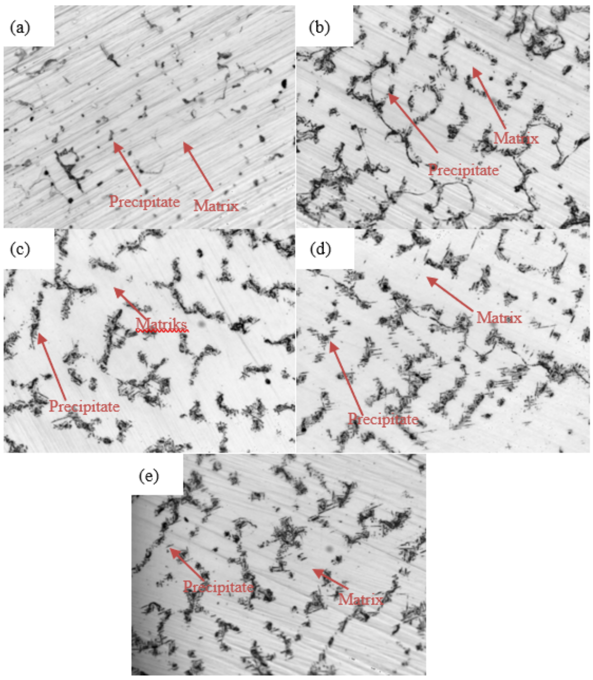

Figure 2. Microstructure using an Optical Microscope magnification of 200X for 0,15C alloy (a) AC, (b) DF, (c) UT, (d) QC, (e) AG.

3.2 Effects of Heat Treatment and Carbon Content on Hardness Properties in Co-Cr-Mo Alloys

Figure 4 demonstrates the enhancement in hardness of the as-cast (AC) material following heat treatment. The heat treatment at 1050°C for 6 hours resulted in minimal variation in hardness values, with similar observations for the aged (AG) specimen treated at 815°C for 6 hours. The AC material exhibited higher hardness values (301.476 HV for 0.08C alloy; 312.688 HV for 0.15C alloy) compared to the furnace-cooled (DF) specimens, which showed the lowest hardness values among all treatments (259.572 HV for 0.08C; 281.412 HV for 0.15C).

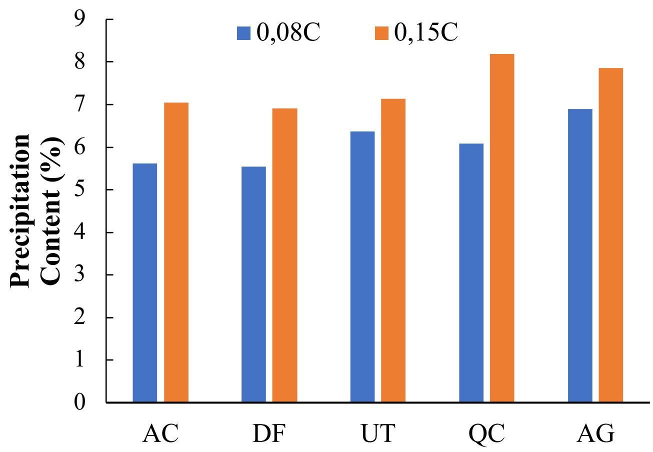

Figure 3. Precipitation content in Co-Cr-Mo alloys under different heat treatment conditions.

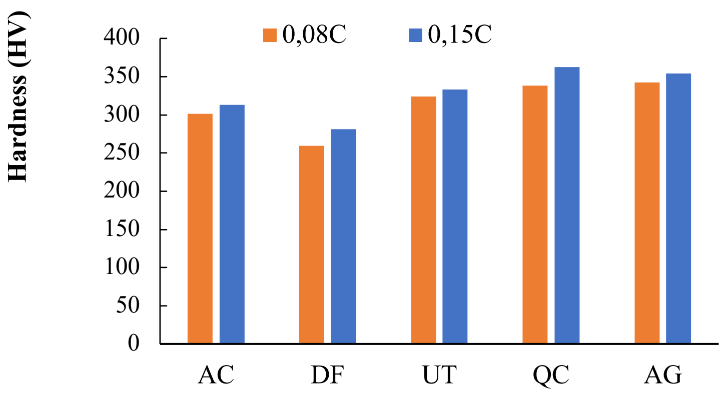

Figure 4. Vickers hardness values of Co-Cr-Mo alloys showing the effects of heat treatment procedure and carbon content (0.08 wt% vs 0.15 wt%).

The reduced hardness in DF specimens can be attributed to microstructural changes during slow cooling. The furnace cooling process facilitated grain growth through dislocation rearrangement, where smaller grains diminished while larger grains expanded [17]. This microstructural coarsening decreases material strength as dislocations become more mobile. In contrast, air-cooled (UT) specimens displayed intermediate hardness values (323.944 HV for 0.08C; 332.782 HV for 0.15C), reflecting the influence of cooling rate on precipitate formation [18]. The quenched (QC) specimens achieved peak hardness values (337.794 HV for 0.08C; 362.562 HV for 0.15C), demonstrating that rapid cooling effectively enhances hardness through refined precipitate distribution [18]. The AG specimens showed substantial hardness (342.698 HV for 0.08C; 353.962 HV for 0.15C) due to fine precipitate formation during aging, particularly through the development of π and ε phases at aging temperatures of 1023-1073 K [19], as corroborated by microstructural observations in Figures 1 and 2.

The data in Figure 4 further reveals two key trends: (1) a consistent positive correlation between cooling rate and hardness, and (2) higher hardness values in 0.15C specimens compared to their 0.08C counterparts. This carbon-dependent behavior stems from increased precipitate formation at higher carbon concentrations (Figure 3). As reported by Sugawara et al. [20], elevated precipitate content directly enhances the strength of Co-Cr-Mo alloys. Carbon serves as both a crucial precipitate-forming element and a carbide stabilizer, primarily generating robust $M_{23}C_6$-type phases that contribute significantly to hardness [15].

3.3 Effects of Heat Treatment and Carbon Content on Wear Resistance in Co-Cr-Mo Alloys

Wear damage on solid surfaces occurs due to the displacement or loss of material resulting from mechanical forces [21]. In this study, Hank’s solution and a 99% alumina disk were used to simulate the human body's plasma environment during wear resistance testing. Figure 5 presents the ion elution rates of Co-Cr-Mo alloys as measured using the Inductively Coupled Plasma (ICP) technique. The graph illustrates the number of ions released into Hank’s solution after wear testing. The results show fluctuations in the elution behavior of different elements. Among the detected elements—Co, Cr, Mo, Si, Mn, and Ni—molybdenum (Mo) and silicon (Si) exhibited the highest elution levels. This is likely due to the strong tendency of Si to form compounds such as intermetallic sigma-phase, which has a tetragonal crystal structure [22]. In addition, a significant amount of cobalt (Co) was eluted, as it is the base metal in Co-Cr-Mo alloys. The atomic radius of Si is similar to that of Co, allowing Si to dissolve into the Co matrix and form a solid solution with other alloying elements like Cr and Mo [22].

Carbon plays a critical role in the formation of precipitates, particularly the $M_{23}C_6$-type carbide phase [8]. It acts as a stabilizing element for $Cr_{23}C_6$ precipitates, classified under the $M_{23}X_6$ phase family. Alloys with higher carbon content (e.g., 0.15C) exhibited lower ion elution compared to lower-carbon alloys (e.g., 0.08C). This improved performance is attributed to the increased wear resistance from carbide presence and elemental carbon strengthening the alloy's microstructure.

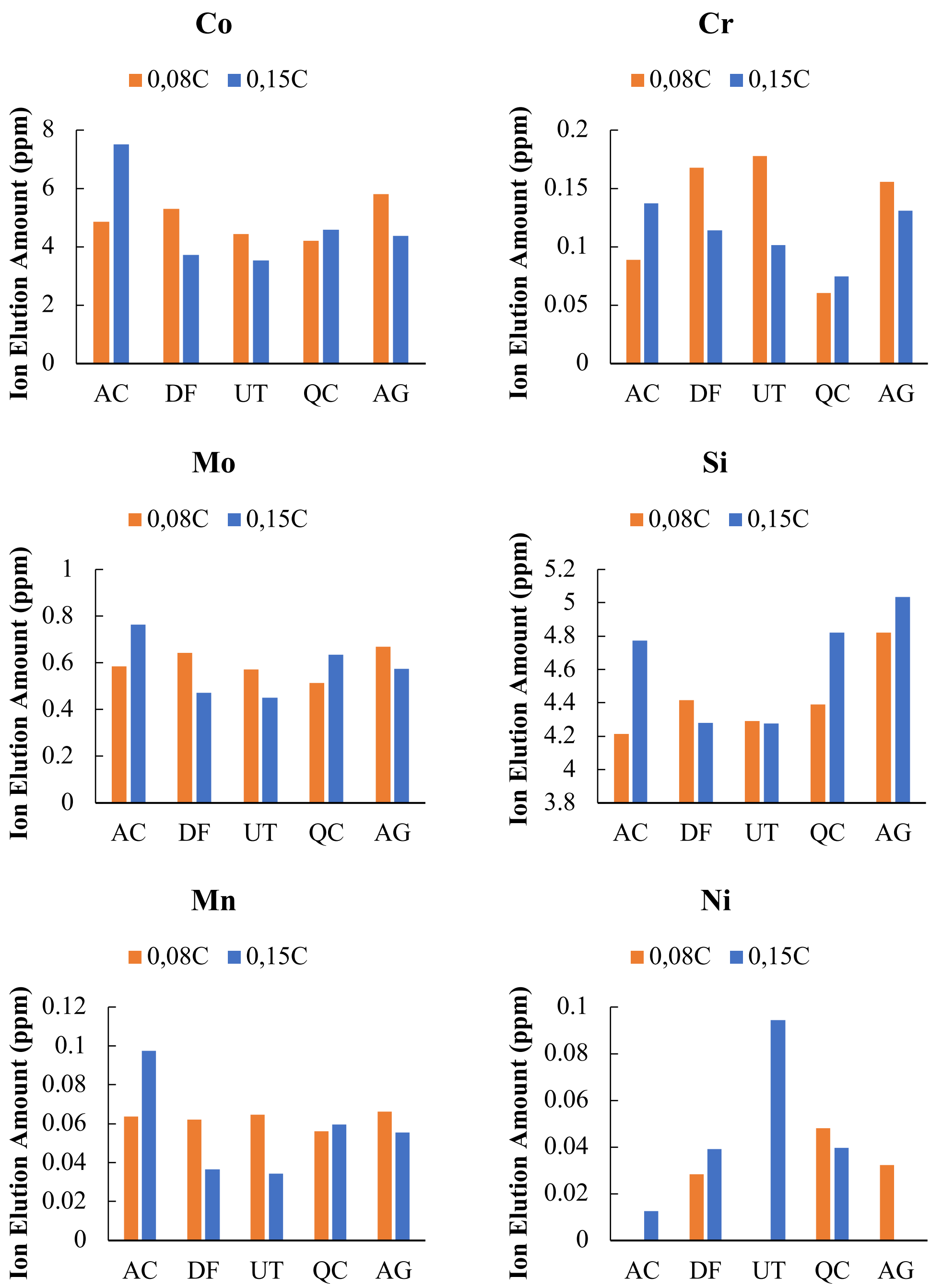

Figure 5. Number of eluted Co, Cr, Mo, Si, Mn, and Ni ions from the Co-Cr-Mo alloy after wear resistance testing in Hank's solution.

As shown in Figure 5, as-cast (AC) specimens generally exhibit higher ion elution rates compared to heat-treated specimens. Figure 6 illustrates the total ion elution into Hank's solution following wear testing. These results confirm that ion release can accelerate wear by disrupting the passive oxide layer on the pin surface, thereby exposing the underlying metal to corrosive fluids [6]. Comparative analysis reveals that the 0.08C alloy tends to release more ions than the 0.15C alloy, indicating inferior wear resistance. Heat treatment significantly influences hardness and, consequently, the wear behavior by altering the alloy's microstructure and enhancing carbide precipitation [12]. In 0.08C alloys, the DF, UT, and QC conditions all resulted in reduced wear resistance. Conversely, 0.15C alloys subjected to the same heat treatment conditions showed improved wear resistance.

Figure 7 (for 0.08C) and Figure 8 (for 0.15C) display SEM images of the worn specimen surfaces. Specimens with higher hardness values generally show improved wear resistance. For example, the QC specimen of the 0.15C alloy, with a hardness of 362.56 HV, showed a lower ion elution value (10.24 ppm) compared to the 0.08C QC specimen with 337.79 HV and 9.31 ppm ion release. However, some studies present a contrasting viewpoint. Wimmer et al. and Chiba et al. argued that complex carbide phases such as $M_{23}C_6$ may actually deteriorate wear performance. This occurs because hard carbides can detach from the surface during sliding, causing three-body abrasive wear [23]. Narushima et al. [24] reported that increasing carbon content can reduce the σ-phase while promoting carbide formation, as carbon reacts with this phase to form $M_{23}X_6$ carbides and η-phase during alloy solidification. Further investigation using Scanning Electron Microscopy–Energy Dispersive X-Ray Spectroscopy (SEM-EDS) was performed to analyze surface damage from wear. Figures 7 and 8 display the surface morphologies after three days of wear testing under various heat treatment conditions and carbon compositions. The worn surfaces exhibit characteristic abrasive wear features, including long, parallel grooves produced by hard particles.

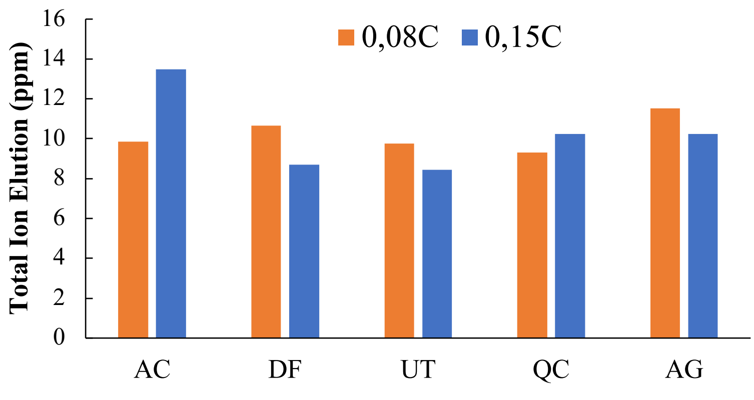

Figure 6. Total amount of precipitate eluted into Hank's solution after the wear resistance test.

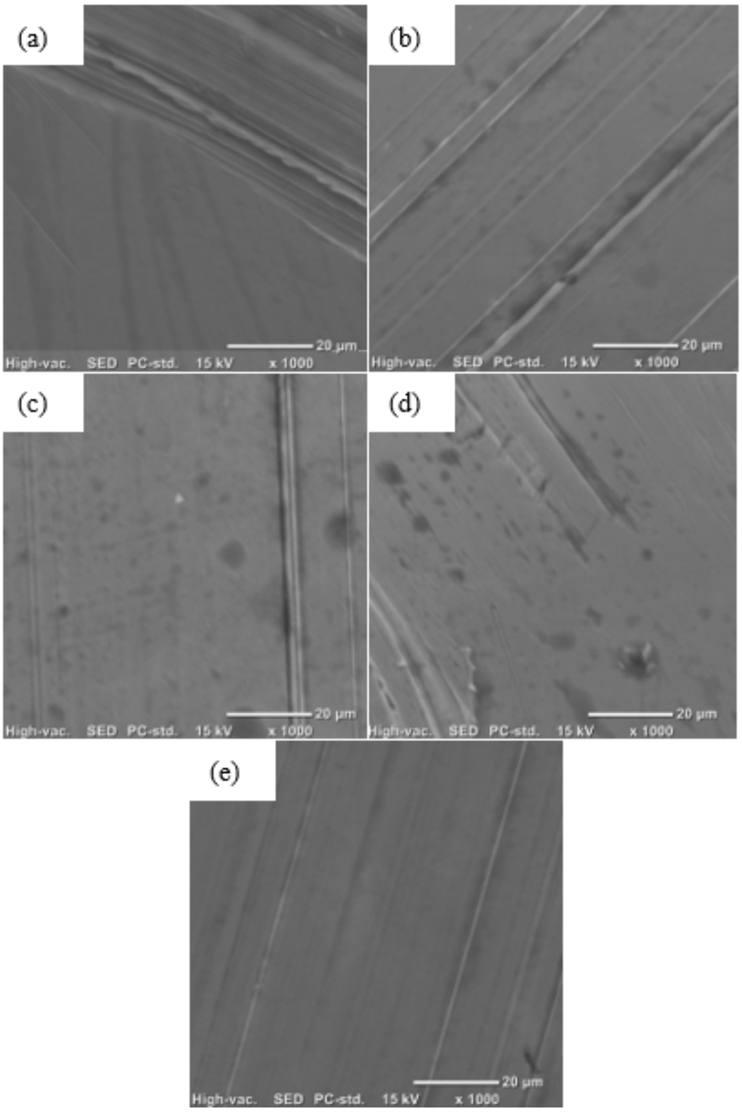

Figure 7. SEM images at 1000× magnification of 0.08C alloy specimens after wear testing: (a) AC, (b) DF, (c) UT, (d) QC, and (e) AG.

For AC and DF specimens of both carbon compositions, visible scratches and indentations aligned with the direction of pin movement are evident (Figures 7a–b and 8a–b). In Figure 7c, two wear grooves can be observed, indicating localized asperity-induced abrasion. The wear tracks reveal particle plowing through the softer matrix, whereas more wear-resistant carbides remain relatively intact. In Figure 8c, the grooves are less pronounced than in Figure 7c, suggesting that higher carbon content contributes to increased surface stability. In contrast, Figure 7d shows irregular grooves and cavities, which may promote higher ion elution rates [6]. Figure 8d displays friction grooves aligned with dark subsurface carbide zones. Meanwhile, Figures 7e and 8e both show wear tracks parallel to the shear direction, consistent with abrasion by hard third-body particles.

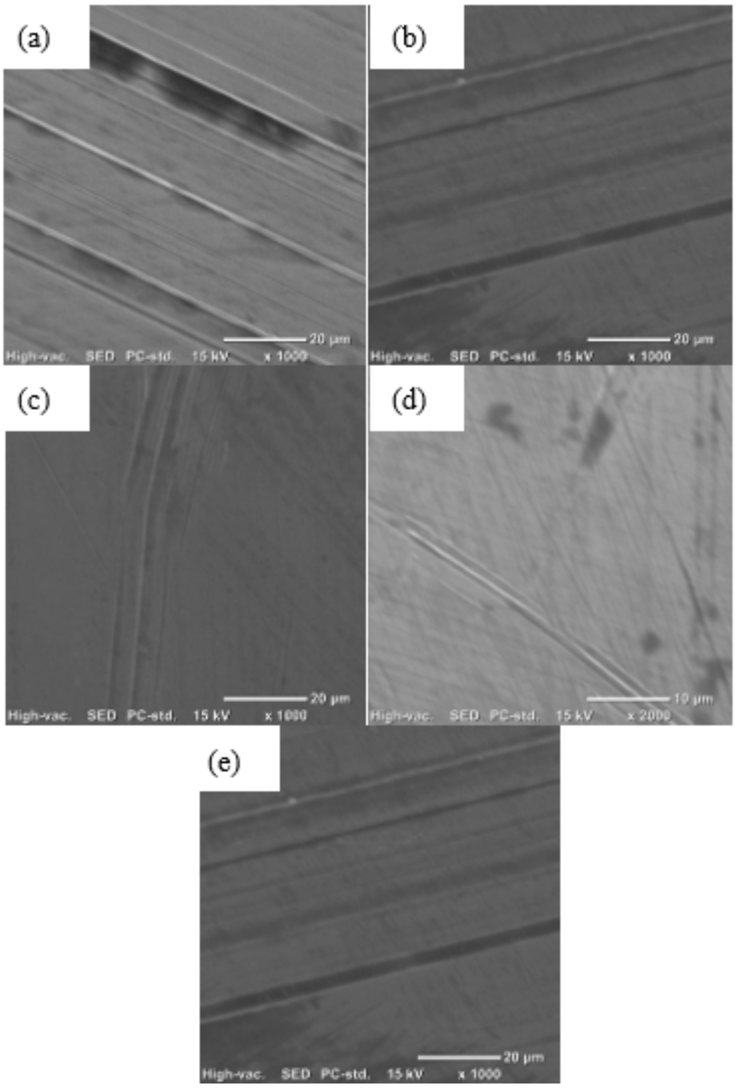

Figure 8. SEM images at 1000× magnification of 0.15C alloy specimens after wear testing: (a) AC, (b) DF, (c) UT, (d) QC, and (e) AG.

4. Conclusion

From the experimental analysis of heat treatment on Co-Cr-Mo-xC alloys (x = 0.08 and 0.15 wt%), the key findings are as follows:

- Heat treatment combined with a high carbon composition increases the hardness of Co-Cr-Mo alloys, primarily due to microstructural changes resulting from increased precipitate formation, which directly contributes to the enhanced hardness levels.
- Although higher carbon content alloys demonstrated increased hardness, the improvement in wear resistance was relatively insignificant compared to lower carbon alloys. This is likely due to the specific phase formations in the specimens that influence tribocorrosion behavior.

- The total ion elution values (in ppm) for the 0.08C alloy, in the order of heat treatment condition—AC, DF, UT, QC, and AG—were 9.7733; 10.6093; 9.5117; 9.2821; and 11.5446, respectively. For the 0.15C alloy, the corresponding values were 13.2959; 8.6582; 8.4881; 10.2249; and 10.1723.
- The as-cast (AC) specimens exhibited a coarse, blocky morphology, whereas heat-treated specimens showed similar morphologies with refined grain structures. The highest hardness value was observed in the 0.15C QC specimen (362.562 HV), while the lowest total ion elution was found in the 0.15C UT specimen (8.4881 ppm).
- Overall, the results indicate that variations in heat treatment and carbon content significantly influence the mechanical and tribological properties of Co-Cr-Mo alloys. These findings support the alloy's suitability for biomedical implant applications, particularly where wear resistance and corrosion performance are critical.

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Conflict of Interests

The authors affirm there are no competing financial interests or organizational influences affecting this work.

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