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Material Microstructure and Mechanical Properties of Spark Plasma-Sintered $\text{Al}_{0.2}\text{CoCrFeNi-5\%WC}$ High-Entropy Alloy Composites: A Sintering Temperature Study

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Abstract

$\text{Al}_{0.2}\text{CoCrFeNi-5\%WC}$ high-entropy alloy (HEA) composites were fabricated via spark plasma sintering at temperatures ranging from 900 °C to 1050 °C, and the effects of sintering temperature on phase constitution, microstructure, and mechanical properties were systematically investigated. The results show that all composites consist predominantly of an FCC matrix, WC, M_{23}C_6 and M_6C carbides. With increasing sintering temperature, interfacial reactions are promoted, leading to the progressive consumption of WC and an increase in carbide content. The composite sintered at 1000 °C achieves the optimal combination of properties, with a relative density of 96.8%, a yield strength of 468 MPa, an ultimate compressive strength of 1871 MPa, and a fracture strain of 43.6%. The outstanding strength–ductility synergy originates from near-full densification, robust interfacial bonding, and multiple carbide strengthening mechanisms. Excessively high sintering temperature (1050 °C) results in reinforcement coarsening and degradation of mechanical properties.

Keywords: high-entropy alloy matrix composites; spark plasma sintering; microstructure; mechanical properties

1. Introduction

Traditional alloy materials are formed on the basis of one or two main metal elements, and small amounts of other elements are added [1,2]. Particularly in load-bearing components under compressive loading, such as cutting tools, die inserts, bearing liners, and mechanical protective coatings, materials are subjected to severe compressive stress and contact stress under long-term service conditions, placing stringent requirements on their compressive strength and ductility. In recent years, traditional alloys have been unable to fully meet the increasingly demanding application scenarios of modern industry, and there is an urgent need to develop comprehensive materials with high high-temperature mechanical strength, excellent thermal fatigue resistance, oxidation resistance and corrosion resistance. Thus, high-entropy alloys (HEAs) emerged [3,4], changing the traditional

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alloy design concept. By mixing five or more metal elements with equal or near equal molar ratios without distinguishing the main elements, the obtained high-entropy alloys not only have a simple structure but also easily generate nanoparticles and amorphous structures with strengthening properties [5–8], showing high strength, high toughness, temper softening resistance, wear resistance and corrosion resistance, making them ideal candidate materials for high-performance protective coatings in aerospace, energy and marine engineering fields. Among various HEA systems, the $\text{Al}_x\text{CoCrFeNi}$ series has attracted extensive research attention due to its tunable microstructure and excellent comprehensive properties. When the Al content is $x = 0.2$, the alloy maintains a single face-centered cubic (FCC) solid solution structure, which exhibits exceptional ductility and good corrosion resistance, making it an ideal matrix material for composite reinforcement. However, the relatively low strength of monolithic $\text{Al}_{0.2}\text{CoCrFeNi}$ HEA limits its application in load-bearing components. To address this limitation, introducing ceramic reinforcing phases to prepare HEA matrix composites has become an effective strategy to simultaneously improve strength and maintain acceptable ductility.

The progress of science and technology has continuously increased the demand for comprehensive material performance. A material with only one outstanding performance can no longer meet that need. Researchers have begun to optimize and combine materials with different characteristics to prepare composite materials with better overall performances [9,10]. With the continuous deepening of high-entropy alloy research [11,12], the development of high-entropy alloy-based composite materials has gradually reached the forefront of composite materials research. Among these materials, ceramic-reinforced high-entropy alloy matrix composites [11,12] exhibit excellent comprehensive properties such as high strength, good plasticity and superior corrosion resistance [13,14]. This type of composite has broad research prospects as wear-resistant and corrosion-resistant coatings for key components, and the performance of bulk composites prepared by SPS in this work can provide important performance benchmarks and a process reference for the development of high-quality coatings of the same system in future studies. The performance of high-entropy alloy-based composites is not only affected by the composition of the high-entropy alloys and the type of strengthening phases but also is closely related to the preparation method. The preparation methods of high-entropy alloy-based composite materials are diverse, mainly including the mechanical alloying method [15,16], hot pressing sintering [17,18], spark plasma sintering [12,19–22], arc melting [21], and induction melting [4,22]. Among them, the spark plasma sintering (SPS) process in powder metallurgy has the advantages of a fast sintering speed, a low sintering temperature, the high relative density of the obtained sintered body, and a high diffusion coefficient. It can effectively avoid the problem of element burning caused by different melting points of alloy elements [23,24] and obtain high entropy alloys with uniform microstructure and excellent mechanical properties.

WC is an ideal reinforcing phase due to its ultra-high hardness, excellent wear resistance, and good chemical compatibility with transition metal HEA matrices. Compared with traditional wear-resistant materials such as Stellite alloys, WC-reinforced HEA composites exhibit higher high-temperature strength, better corrosion resistance, and lower material cost, while maintaining good processability. In summary, the high-entropy alloy-based composite materials have broad application prospects, especially in high-temperature and high-strength environments with enormous potential for application. While $\text{Al}_{0.2}\text{CoCrFeNi}$ and WC have been studied individually, the systematic effect of a continuous temperature gradient 900–1050 °C on the coupled evolution of the $\text{WC} \rightarrow \text{M}_6\text{C}/\text{M}_{23}\text{C}_6$ transformation and the resultant mechanical properties in this specific composite system has not been previously reported. Understanding this relationship in bulk SPS composites is a prerequisite for optimizing the SPS parameters for coating applications, where similar

densification and interfacial reaction mechanisms govern the quality and performance of the deposited layer. Thus, this study investigates the effect of the sintering temperature on the microstructures and mechanical properties of the $\text{Al}_{0.2}\text{CoCrFeNi}$ -5%WC high-entropy alloy-based composite. This not only helps to gain a deeper understanding of the relationship between material structure and properties but also provides important theoretical guidance for optimizing the preparation process of bulk composites and the subsequent development of high-performance coatings of the same system, promoting their applications in aerospace, energy and other fields as both structural materials and protective coatings.

2. Materials and Methods

2.1. Experiment Materials

$\text{Al}_{0.2}\text{CoCrFeNi}$ pre-alloyed powder with a purity greater than 99.9% and a particle size of 45–105 μm was selected as the HEA matrix material. The powder was prepared by argon gas atomization and purchased from Beijing Xingrongyuan Technology Co., Ltd., Beijing, China. WC nanopowder with a diameter of 200 nm and a purity of 99.99% was supplied by Shanghai Chaowei Nanotechnology Co., Ltd., Shanghai, China. Before the experiment, a total mass of 20 g of mixed powder was prepared for each batch, and a high-precision electronic balance (with an accuracy of 0.0001 g) was used to weigh $\text{Al}_{0.2}\text{CoCrFeNi}$ high entropy alloy and WC ceramic particle powder, respectively. The weighed powder was put into a stainless-steel ball milling jar with stainless-steel grinding balls; the ratio of ball to material was 10:1. To prevent powder oxidation or cold welding during ball milling, anhydrous ethanol was added as the grinding medium in the ball milling tank. An SFM-I planetary ball mill was used to mill the mixed powder at a speed of 300 r/min and a ball milling time of 2 h. After ball milling, the alloy powder was filtered and dried in a vacuum drying oven for 5 h to remove residual anhydrous ethanol from the powder.

2.2. Preparation and Analysis

The spark plasma sintering (SPS) method was used to prepare $\text{Al}_{0.2}\text{CoCrFeNi}$ -5%WC high entropy alloy composite material. The SPS furnace was designed and manufactured by Shanghai Chenhua Technology Co., Ltd. It had a maximum sintering temperature of 2300 $^{\circ}\text{C}$, a maximum loading force of 2 t, an extreme vacuum degree of 10^{-4} Pa, rated power of 20 kW, an input current of 0–2000 A, and an input voltage of 0–10 V. The mixed powder was placed into a graphite mold with an inner diameter of 20 mm. A tablet press was used to pre-press the powder; then, the mold was placed into an SPS sintering furnace for sintering. The sintering temperature was measured using a pyrometer focused on the graphite die surface. Temperature control was achieved via a PID controller with a heating rate of 100 $^{\circ}\text{C}/\text{min}$, with a holding time at each target temperature of 10 min. The sintering temperatures were 900 $^{\circ}\text{C}$, 950 $^{\circ}\text{C}$, 1000 $^{\circ}\text{C}$, 1050 $^{\circ}\text{C}$, respectively. After sintering, the composite material was taken out, and sandpaper was used to polish the graphite paper on the upper and lower surfaces of the $\text{Al}_{0.2}\text{CoCrFeNi}$ -5%WC composite material to make it smooth and clean. The schematic diagram of the SPS experimental setup is provided in Figure 1.



Figure 1. Spark plasma sintering equipment.

An Empyrean X-ray diffractometer (XRD) produced by Panaco in the Netherlands was used for the phase analysis of the $\text{Al}_{0.2}\text{CoCrFeNi-5\%WC}$ composite materials. Before this experiment, the surfaces of the samples were polished with sandpaper and cleaned with alcohol. Cu target $\text{K}\alpha$ Radiation (wavelength) was adopted, with a working voltage of 40 kV, a working current of 40 mA, a scanning angle of $20\text{--}100^\circ$, and a scanning speed of $4^\circ/\text{min}$. The microstructure analysis was conducted using a JXA-8530F PLUS electron probe micro-analyzer (EPMA) produced by Japan Electronics, equipped with an energy-dispersive spectroscopy (EDS) detector for compositional analysis. The MT-50 Vickers hardness tester was used to test the hardness of the samples. Before the experiment, the surfaces of the samples were polished to ensure the parallelism of the upper and lower surfaces. The test load and holding time were set to 10 N and 15 s, respectively. To reduce errors, the hardness of every sample was tested at least six times, and the average value was taken as the final hardness of the $\text{Al}_{0.2}\text{CoCrFeNi-5\%WC}$ composite material. The densities of the sintered composites were measured using the Archimedes method. Each sample was measured three times, and the average density is reported. The relative density was calculated as the ratio of the measured density to the theoretical density. Uniaxial compression tests were performed at room temperature using a universal testing machine (UTM-5305, Shenzhen Suns Technology Co., Ltd., Shenzhen, China) with a strain rate of $1 \times 10^{-3} \text{ s}^{-1}$. Cylindrical specimens of $\text{Ø}4 \text{ mm} \times 8 \text{ mm}$ were used. Three samples per condition were tested.

3. Results and Discussion

The $\text{Al}_{0.2}\text{CoCrFeNi}$ high-entropy alloy prepared by the aerosolization method was used as the matrix material. Here, 5 vol.% WC was added and subsequently ball milled for 2 h. The effect of different sintering temperatures on the microstructure and mechanical property of $\text{Al}_{0.2}\text{CoCrFeNi-5\%WC}$ high-entropy alloy-based composite materials was investigated by spark plasma sintering.

3.1. Phase Constitution

Figure 2a shows the XRD patterns of $\text{Al}_{0.2}\text{CoCrFeNi-5\%WC}$ composites prepared at different sintering temperatures, while Figure 2b shows an enlarged XRD pattern at a diffraction angle of $30\text{--}60^\circ$. The phase assembly remains qualitatively consistent across all

sintering temperatures, comprising a primary face-centered cubic (FCC) solid solution matrix, residual WC reinforcement, $M_{23}C_6$ and M_6C carbides. Notably, as the sintering temperature increases, the diffraction peak intensities of the M_6C and $M_{23}C_6$ phases increase progressively, whereas the characteristic peaks of the WC phase exhibit a concomitant diminution. This trend unequivocally indicates that elevated temperatures promote the interfacial reaction between the WC particles and the constituent elements of the HEA matrix. The driving force for this interfacial reaction is fundamentally thermodynamic in origin. The highly negative mixing enthalpies of C with W $-60 \text{ kJ}\cdot\text{mol}^{-1}$ and Cr $-61 \text{ kJ}\cdot\text{mol}^{-1}$ provide a strong chemical affinity for the formation of both W-rich and Cr-rich carbides [25]. The SPS process, characterized by the simultaneous application of uniaxial pressure and pulsed direct current, generates localized Joule heating at particle contacts. This non-equilibrium thermal activation facilitates the decomposition of WC and the subsequent diffusion of W and C atoms into the adjacent FCC matrix. The observed consumption of WC and concomitant precipitation of M_6C and $M_{23}C_6$ carbides are consistent with a reactive diffusion mechanism. The high density of crystalline defects introduced during ball milling significantly accelerates atomic transport during spark plasma sintering (SPS). Quantitative microstructural analysis shows that the dislocation density in the as-milled powder reaches approximately $1.8 \times 10^{15} \text{ m}^{-2}$, which is one to two orders of magnitude higher than that in the as-atomized powder (10^{13} – 10^{14} m^{-2}), confirming the critical role of defect-enhanced diffusion in driving the interfacial reactions.

The crystallographic parameters and quantitative results of each phase are presented in Table 1. As shown, the lattice constant of the FCC matrix increases linearly from $3.578 \pm 0.002 \text{ \AA}$ at 900°C to $3.588 \pm 0.002 \text{ \AA}$ at 1050°C . This lattice expansion is attributed to the dissolution of W and C atoms into the FCC matrix, whose larger atomic radii induce lattice distortion, further confirming the interfacial reaction and elemental diffusion between WC and the matrix. The lattice constants of M_6C and $M_{23}C_6$ carbides decrease slightly with increasing sintering temperature, which arises from the partial substitution of Cr atoms in the carbide lattices by Fe, Co and Ni atoms with smaller atomic radii. This minor change (less than 0.3%) indicates that both carbides are thermodynamically stable phases with no fundamental change in their crystal structures. In addition, the dislocation density decreases from $8.7 \times 10^{14} \text{ m}^{-2}$ to $3.2 \times 10^{13} \text{ m}^{-2}$ with increasing temperature, indicating significant dislocation annihilation during sintering.

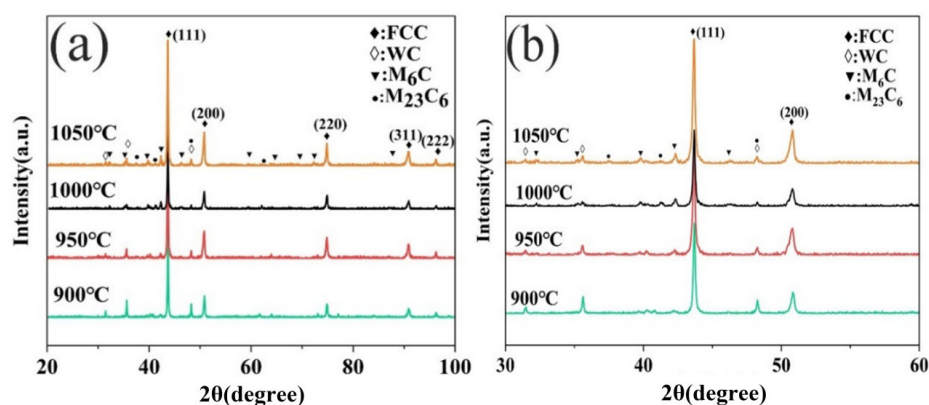


Figure 2. XRD results of $\text{Al}_{0.2}\text{CoCrFeNi-5\%WC}$ composites: (a) XRD pattern; (b) the enlargement of the XRD pattern at $2\theta = 30$ – 60° .

Table 1. Crystallographic data of Al_{0.2}CoCrFeNi-5%WC composite materials at different sintering temperatures.

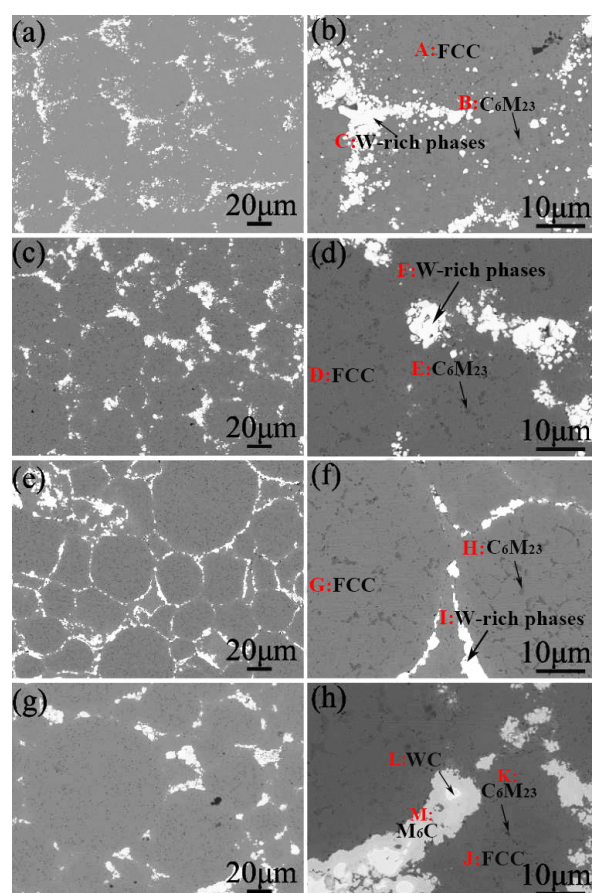
Temperature (°C)	Phase	Main Diffraction Peak Position 2θ/Degree	Corresponding Crystal Plane (hkl)	Lattice Constant
900	FCC	43.42, 50.55, 74.58, 90.34	(111), (200), (220), (311)	a = 3.578 ± 0.002
	WC	31.52, 35.68, 48.32	(001), (100), (101)	a = 2.906, c = 2.837
	M ₂₃ C ₆	37.85, 48.32, 62.52	(331), (420), (511)	a = 10.64 ± 0.02
	M ₆ C	40.85, 43.52, 60.96	(311), (400), (440)	a = 10.92 ± 0.03
950	FCC	43.38, 50.48, 74.52, 90.28	(111), (200), (220), (311)	a = 3.582 ± 0.002
	WC	31.48, 35.62, 48.26	(001), (100), (101), (110)	a = 2.906, c = 2.837
	M ₂₃ C ₆	37.82, 48.28, 62.43	(331), (420), (511)	a = 10.63 ± 0.02
	M ₆ C	40.82, 43.49, 60.94	(311), (400), (440)	a = 10.91 ± 0.03
1000	FCC	43.32, 50.42, 74.46, 90.22	(111), (200), (220), (311)	a = 3.586 ± 0.002
	WC	31.45, 35.58, 48.20	(001), (100), (101), (110)	a = 2.906, c = 2.837
	M ₂₃ C ₆	37.78, 48.22, 62.36	(331), (420), (511)	a = 10.62 ± 0.02
	M ₆ C	40.78, 43.47, 60.89	(311), (400), (440)	a = 10.90 ± 0.03
1050	FCC	43.28, 50.38, 74.40, 90.18	(111), (200), (220), (311)	a = 3.588 ± 0.002
	WC	31.42, 35.54, 48.16	(001), (100), (101), (110)	a = 2.906, c = 2.837
	M ₂₃ C ₆	37.75, 48.19, 62.32	(331), (420), (511)	a = 10.61 ± 0.02
	M ₆ C	40.75, 43.42, 60.84	(311), (400), (440)	a = 10.89 ± 0.03

3.2. Microstructure

Backscattered electron (BSE) micrographs combined with energy-dispersive spectroscopy (EDS) compositional analysis are employed to systematically characterize the microstructural evolution of Al_{0.2}CoCrFeNi-5%WC high-entropy alloy (HEA) composites consolidated via spark plasma sintering at varying temperatures, and the obtained results are shown in Figure 3 and Table 2. It can be seen that a well-defined multi-phase contrast hierarchy is clearly resolved across all fabricated samples. Specifically, the continuous grey matrix phase is identified as the face-centered cubic (FCC)-structured Al_{0.2}CoCrFeNi HEA. For the sample sintered at 1000 °C, the matrix has an average composition of 4.08 at.% Al, 24.70 at.% Co, 21.30 at.% Cr, 24.78 at.% Fe, 24.38 at.% Ni, 0.49 at.% W and 0.27 at.% C (Table 2, Region G). The slight enrichment of W and C in the matrix directly verifies the limited dissolution of WC particles into the HEA matrix during the SPS process. The deep grey precipitates are confirmed as Cr-rich M₂₃C₆ carbides, with a measured composition of 0.88 at.% Al, 7.12 at.% Co, 54.62 at.% Cr, 10.15 at.% Fe, 6.12 at.% Ni, 0.19 at.% W and 20.92 at.% C at 1000 °C (Table 2, Region H). The presence of Fe, Co and Ni in the carbide lattice indicates the partial substitution of Cr atoms by these matrix elements during the interfacial reaction. While the bright white phase located at the matrix particle interfaces is the W-rich reinforcing constituent, which consists of both unreacted WC cores (44.85 at.% W and 36.05 at.% C at 1000 °C, Table 2, Region I) and interfacial reaction-generated W-rich M₆C carbides with a general formula of (Fe,Co,Ni,W)₆C, corresponding to a composition of 2.02 at.% Al, 14.32 at.% Co, 20.12 at.% Cr, 12.05 at.% Fe, 9.38 at.% Ni, 25.75 at.% W and 16.36 at.% C at 1050 °C (Table 2, Region M).

Table 2. EDS results of Al_{0.2}CoCrFeNi-5%WC composites (regions in Figure 3) prepared at different temperatures(at.%).

Temperature (°C)	Region	Al	Co	Cr	Fe	Ni	W	C
900	overall	4.30	22.50	22.35	22.62	22.83	2.75	2.65
	A	4.32	23.48	24.32	23.57	23.27	0.28	0.76
	B	1.85	10.22	48.36	12.15	8.62	0.32	18.48
	C	2.68	5.36	8.25	5.89	4.22	38.65	34.95
950	overall	4.15	22.85	22.38	22.86	22.37	2.95	2.44
	D	4.16	24.70	21.76	24.18	23.84	0.73	0.63
	E	1.25	8.36	52.18	10.92	7.25	0.24	19.80
	F	2.25	4.85	6.92	5.12	3.68	42.36	34.82
1000	overall	3.98	23.40	22.43	22.49	22.52	2.98	2.20
	G	4.08	24.70	21.30	24.78	24.38	0.49	0.27
	H	0.88	7.12	54.62	10.15	6.12	0.19	20.92
	I	2.10	3.95	5.68	4.25	3.12	44.85	36.05
1050	overall	3.75	22.78	23.73	22.80	22.72	3.24	2.98
	J	3.94	25.20	19.92	25.24	24.94	0.16	0.60
	K	0.67	6.56	56.75	9.74	5.54	0.15	20.59
	L	...	2.19	1.87	1.86	2.23	45.15	46.70
	M	2.02	14.32	20.12	12.05	9.38	25.75	16.36

**Figure 3.** Backscatter images of Al_{0.2}CoCrFeNi-5%WC composites prepared at different temperatures: (a,b) 900 °C; (c,d) 950 °C; (e,f) 1000 °C; (g,h) 1050 °C.

The microstructural evolution of the composites with increasing sintering temperature exhibits a strong correlation with the densification mechanism and interfacial reaction kinetics of the SPS process. As shown in Table 2, with increasing sintering temperature from 900 °C to 1050 °C, the W content in the FCC matrix first increases from 0.28 at.%

to 0.73 at.% (950 °C) and then decreases to 0.16 at.% (1050 °C), while the Cr content in $M_{23}C_6$ carbides increases progressively from 48.36 at.% to 56.75 at.%. These trends further confirm that elevated temperatures promote the decomposition of WC and the subsequent formation of M_6C and $M_{23}C_6$ carbides via interfacial reactions. At the lowest sintering temperature of 900 °C, the composite obtains a relatively low relative density of only 85.7%, with a low fraction of $M_{23}C_6$ precipitation, prominent residual porosity, which is attributed to the insufficient thermal activation energy at this temperature, leading to a limited atomic diffusion rate that fails to support effective viscous flow, diffusion-mediated neck growth, pore elimination, and robust interfacial bonding, with the restricted interfacial reactions also kinetically constrained at such a low temperature. As the sintering temperature rises to 950 °C, the coupled effect of elevated temperature and axial pressure during SPS enhances particle rearrangement and plastic deformation, while the pulsed DC current generates localized high temperatures at particle contacts, collectively promoting densification and interfacial diffusion. Thus, the relative density of the composite increases to 94.2%. When the sintering temperature reaches 1000 °C, the composite achieves a near-full relative density of 96.8%, with a defect-free microstructure, no visible cracks or pores at the WC–matrix interface, and excellent interfacial bonding that is critical for efficient load transfer from the HEA matrix to the reinforcing particles; meanwhile, the $M_{23}C_6$ precipitates are uniformly distributed along the grain boundaries to form a semi-continuous carbide network, which can effectively pin grain boundaries and inhibit matrix grain growth during sintering, and this microstructural feature also indicates that the precipitation of $M_{23}C_6$ occurs concurrently with matrix grain growth and pore closure. However, a further increase in sintering temperature to 1050 °C only brings a marginal improvement in the relative density to 97.2% but induces pronounced adverse microstructural degradation. The bright white W-rich reinforcing phases undergo significant coarsening and agglomeration: the average carbide size increases from $2.17 \pm 0.12 \mu\text{m}$ at 1000 °C to $6.15 \pm 0.21 \mu\text{m}$ at 1050 °C, transitioning from a fine semi-continuous boundary layer to coarse, isolated clusters, as the elevated temperature drastically increases the diffusion rate of W atoms and promotes the Ostwald ripening of the carbide phases. The area fraction of W-rich phases also increases from $18.7 \pm 1.4\%$ to $21.3 \pm 1.5\%$ with the temperature rise, due to the intensified interfacial reaction that consumes residual WC, and such coarsening of the reinforcing particles will reduce their specific surface area, weaken their strengthening effect, and ultimately impair the load-bearing efficiency of the reinforcement phase in the composite.

3.3. Mechanical Properties

Figure 4 displays the engineering compressive stress–strain curves of $\text{Al}_{0.2}\text{CoCrFeNi-5\%WC}$ composites sintered at different temperatures, and the corresponding mechanical performance parameters are summarized in Table 3. The mechanical properties of the composites are strongly dependent on the sintering temperature, which directly governs their densification behavior and microstructural evolution. At 900 °C, the composite achieves only a low relative density of 85.7%, corresponding to an image-analyzed porosity fraction of $9.3 \pm 0.2\%$, which acts as severe stress concentration sites that accelerate crack initiation and propagation, leading to premature brittle fracture under compression. Consequently, it exhibits a yield strength of merely 202 MPa, an ultimate compressive strength of 253 MPa, and a fracture strain as low as 4.4%. When the sintering temperature is increased to 950 °C, enhanced atomic diffusion and plastic yielding under spark plasma sintering (SPS) pressure promote significant densification with the relative density rising to 94.2%, and the improved densification and interfacial bonding facilitate more effective load transfer from the ductile high-entropy alloy (HEA) matrix to the hard WC particles, resulting in a substantial increase in yield strength to 457 MPa and Vickers hardness from

162 HV to 198 HV. The composites sintered at 950 °C and 1050 °C did not fracture under the maximum compressive load, indicating superior plastic deformation capability. It should be noted that the compression test machine used in this work has a maximum displacement limit, corresponding to a maximum applied strain of 50%. The ultimate compressive strength and fracture strain of these two samples could not be determined under the present test conditions, as no fracture occurred within the applied strain limit. We have applied the standard true stress–strain conversion to the measured engineering stress–strain data for these samples, to correct the effect of area change during plastic deformation. Notably, the composite sintered at 1000 °C attains the optimal comprehensive mechanical properties, with a relative density of 96.8%, a yield strength of 468 MPa, an ultimate compressive strength of 1871 MPa, a fracture strain of 43.6%, and a Vickers hardness of 226 HV. This outstanding strength–ductility synergy originates from the synergistic effects of multiple strengthening mechanisms: (1) load transfer strengthening enabled by robust defect-free matrix–reinforcement interfaces; (2) grain boundary strengthening via grain-boundary pinning by in situ precipitated M_6C and $M_{23}C_6$ carbides; (3) Orowan strengthening arising from finely dispersed carbides with an average size of $2.17 \pm 0.12 \mu\text{m}$ and an interparticle spacing of $4.92 \pm 0.1 \mu\text{m}$ that effectively impede dislocation motion; and (4) solid solution strengthening induced by lattice distortion from dissolved W and C atoms in the HEA matrix.

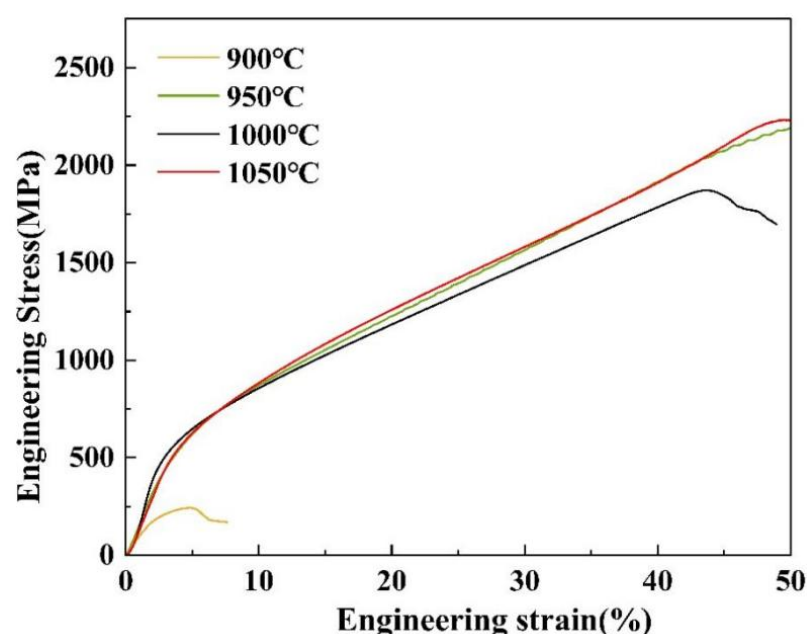


Figure 4. Engineering compressive stress–strain curves of $\text{Al}_{0.2}\text{CoCrFeNi-5\%WC}$ composites prepared at different temperatures.

Table 3. Mechanical properties of $\text{Al}_{0.2}\text{CoCrFeNi-5\%WC}$ composites prepared at different temperatures.

Temperature (°C)	Density (g/cm ³)	Relative Density (%)	σ_y (MPa)	$\sigma_{\max}$ (MPa)	ϵ_f (%)	Vickers Hardness (HV)
900	7.13 ± 0.01	85.7 ± 0.2	202 ± 18	253 ± 9	4.4 ± 0.5	162 ± 23
950	8.01 ± 0.03	94.2 ± 0.4	457 ± 23	-	-	198 ± 10
1000	8.05 ± 0.04	96.8 ± 0.5	468 ± 8	1871 ± 22	43.6 ± 0.6	226 ± 10
1050	8.09 ± 0.02	97.2 ± 0.3	452 ± 15	-	-	238 ± 6

To quantitatively verify the contributions of these strengthening mechanisms, the total yield strength of the composite is expressed as the linear superposition of individual strengthening contributions, a widely accepted approximation for particle-reinforced metal matrix composites [26,27]:

$$\sigma_y = \sigma_0 + \sigma_{ss} + \sigma_{gb} + \sigma_{Orowan} + \sigma_{LT} \quad (1)$$

where σ_0 is the intrinsic lattice friction strength of the $\text{Al}_{0.2}\text{CoCrFeNi}$ matrix, σ_{ss} is the solid solution strengthening contribution, σ_{gb} is the grain boundary strengthening contribution, σ_{Orowan} is the Orowan strengthening contribution from dispersed carbides, and σ_{LT} is the load transfer strengthening contribution from the reinforcing phases.

(1) Intrinsic lattice friction strength (σ_0): The intrinsic lattice friction strength of the $\text{Al}_{0.2}\text{CoCrFeNi}$ FCC matrix at room temperature was taken as 125 MPa, and the uncertainty associated with this value is estimated to be ± 5 MPa, based on the scatter, in the reported literature data [26].

(2) Solid solution strengthening (σ_{ss}): Solid solution strengthening arises from lattice distortion caused by dissolved W and C atoms. For dilute solutes in FCC metals, the Labusch model was employed: $\sigma_{ss} = k_{ss} \cdot c^{2/3}$, where $k_{ss} = 180 \text{ MPa} \cdot (\text{at.}\%)^{(-2/3)}$ is the solid solution strengthening coefficient for W in $\text{Al}_{0.2}\text{CoCrFeNi}$ [27], and $c = 0.49 \text{ at.}\%$ is the measured W content in the matrix (Table 2, Region G). The contribution from interstitial C atoms (0.27 at.%) is estimated to be 5 MPa. Summing these gives $\sigma_{ss} \approx 35 \text{ MPa}$, with an uncertainty of $\pm 4 \text{ MPa}$.

(3) Grain boundary strengthening (σ_{gb}): Grain boundary strengthening follows the classical Hall–Petch relationship: $\sigma_{gb} = k_{HP} \cdot d^{(-1/2)}$, where $k_{HP} = 480 \text{ MPa} \cdot \mu\text{m}^{(1/2)}$ is the Hall–Petch coefficient for $\text{Al}_{0.2}\text{CoCrFeNi}$ [27], and $d = 7.9 \pm 0.3 \mu\text{m}$ is the average matrix grain size measured by the linear intercept method from Figure 3e,f. Substituting these values gives $\sigma_{gb} \approx 170 \text{ MPa}$, with an uncertainty of $\pm 6 \text{ MPa}$ from grain size measurement error.

(4) Orowan strengthening (σ_{Orowan}): Orowan stress for non-shearable carbide particles is calculated as $\sigma_{Orowan} = [0.13Gb / (2\pi(1-\nu)^{(1/2)})] \cdot [\ln(2r/b) / (\lambda - 2r)]$, where $G = 80 \text{ GPa}$ (shear modulus of $\text{Al}_{0.2}\text{CoCrFeNi}$ [26]), $b = 0.254 \text{ nm}$ (Burgers vector, calculated as $a/\sqrt{2}$ with $a = 3.586 \text{ \AA}$ from Table 1), $\nu = 0.3$ (Poisson's ratio [26]), $r = 1.085 \mu\text{m}$ (average carbide radius, $2.17 \pm 0.12 \mu\text{m}$ diameter), and $\lambda = 4.92 \pm 0.1 \mu\text{m}$ (average interparticle spacing from image analysis). This yields $\sigma_{Orowan} \approx 58 \text{ MPa}$, with an uncertainty of $\pm 5 \text{ MPa}$.

(5) Load transfer strengthening (σ_{LT}): The modified shear lag model (Nardone and Prewo) for particulate composites was used: $\sigma_{LT} = 0.5 \cdot V_f \cdot \sigma_m$, where $V_f = 18.7 \pm 1.4\%$ is the total volume fraction of reinforcing phases from quantitative image analysis, and $\sigma_m = 295 \text{ MPa}$ is the yield strength of $\text{Al}_{0.2}\text{CoCrFeNi}$ [28]. This gives $\sigma_{LT} \approx 81 \text{ MPa}$, with an uncertainty of $\pm 7 \text{ MPa}$.

Summing these contributions gives a theoretical yield strength of $469 \pm 15 \text{ MPa}$, which is in excellent agreement with the experimental value of $468 \pm 8 \text{ MPa}$. This suggests that grain boundary strengthening and load transfer strengthening are the dominant contributors to the excellent mechanical properties of the composite.

Further raising the sintering temperature to 1050°C yields the highest relative density (97.2%) and Vickers hardness (238 HV), which is attributed to the intensified interfacial reactions that generate more hard carbides. However, the yield strength decreases slightly to 452 MPa, primarily due to the pronounced coarsening and agglomeration of W-rich reinforcing phases (as observed in Figure 3g,h). Similar to the 950°C sample, the 1050°C sample also did not fracture at 50% strain. The exceptional ductility of the 1050°C sample arises from (1) the transformation of brittle WC to more ductile M_6C carbides, which can better accommodate the transformation of brittle WC to more ductile M_6C carbides, which may contribute to improved plastic deformation behavior before fracture, and (2) the coarsened isolated carbides are less prone to forming continuous crack propagation paths

compared to the semi-continuous network in the 1000 °C sample. Overall, 1000 °C is determined as the optimal sintering temperature for the present composite, as it achieves near-full densification and homogeneous distribution of reinforcing phases, thus delivering the best balance of strength and plasticity. It has important guiding significance for the preparation of Al_{0.2}CoCrFeNi-WC composite coatings. The robust interfacial bonding between WC and HEA matrix and the uniform distribution of fine carbides observed in this bulk study are expected to be favorable factors for achieving high bonding strength and excellent wear resistance in subsequent coating development. The interfacial reaction mechanism revealed in this study can be used to regulate the phase composition and microstructure of the coatings during laser cladding or plasma spraying processes, so as to further improve the service performance of the coatings.

4. Conclusions

In this work, Al_{0.2}CoCrFeNi-5%WC high-entropy alloy matrix composites were successfully prepared by spark plasma sintering at different temperatures, and the relationship between the sintering temperature, microstructure evolution and mechanical properties was systematically established. The main conclusions are as follows:

1. All composites consist of an FCC matrix, residual WC, and in situ M₆C and M₂₃C₆ carbides. A higher sintering temperature promotes interfacial reactions, increasing the carbide content at the expense of the WC.
2. The relative density increases from 85.7% (900 °C) to 97.2% (1050 °C). The composite sintered at 1000 °C achieves a low-porosity microstructure (porosity fraction: $3.2 \pm 0.5\%$) with robust interfaces and a semi-continuous carbide network, where the average carbide size is $2.17 \pm 0.12 \mu\text{m}$, and the area fraction of W-rich phases is $18.7 \pm 1.4\%$. At 1050 °C, W-rich phases coarsen significantly to an average size of $6.15 \pm 0.21 \mu\text{m}$ due to Ostwald ripening, with their area fraction increasing to $21.3 \pm 1.5\%$.
3. Optimal mechanical properties are obtained at 1000 °C. The yield strength is 468 MPa, the ultimate compressive strength is 1871 MPa, the fracture strain is 43.6%, and the Vickers hardness is 226 HV. This strength–ductility synergy mainly arises from load transfer and grain boundary pinning strengthening.
4. The optimal sintering temperature is 1000 °C, balancing densification and interfacial reactions. WC nanoparticle addition combined with optimized SPS is an effective strategy for high-performance HEA matrix composites. The results provide an important theoretical basis and process reference for the subsequent development of Al_{0.2}CoCrFeNi-WC high-performance protective coatings, showing promising application potential in aerospace and energy fields as bulk structural materials, as well as fundamental guidance for the follow-up exploration of this system as coating materials.

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