INVESTIGATION OF INTERACTION OF HIGH-ENTROPY ALLOY WITH INDUSTRIAL REFRACTORY CERAMICS

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Abstract

High-entropy alloys (HEAs) have gained significant attention among researchers due to their exceptional mechanical properties (including high hardness, strength and wear resistance), corrosion and oxidation resistance. The combination of these properties, along with good thermal stability, enables a considerable range of potential applications for HEAs. During the production and processing of HEAs, direct contact with refractory ceramic substrates is frequently encountered. However, research on the interactions between these substrates and HEAs remains limited. The present study aims to characterize the interactions between Ni-Fe-Co-Cr high-entropy alloy and industrial ceramic substrates with Al_2O_3 (68.1–84.7 wt%) and SiO_2 (12.9–25.8 wt%) as main components. The interaction was quantitatively described using contact angle measurements and evaluated through the axisymmetric drop shape analysis (ADSA) method, specifically utilizing the sessile drop technique. The experiments were conducted within the CLASIC high-temperature observation furnace. This approach enables the determination of wetting characteristics at elevated temperatures up to 1,600 °C. To prevent oxidation, the experiments were carried out in varying experimental conditions. The measurements were conducted either in a vacuum or under a slight overpressure of high-purity argon (> 99.9999 %). To gain further insights into the interfacial interactions, comprehensive post-experimental analyses of the HEA and ceramic substrates were performed. This included Scanning Electron Microscopy (SEM) for morphological evaluation and Energy-Dispersive Spectroscopy (EDX) microanalysis of chemical composition.

Keywords: High-entropy alloy, interfacial interactions, wettability, sessile drop method

1. INTRODUCTION

High-entropy alloys are distinguished materials known for their unique composition and properties. Defined by the presence of five or more principal metallic elements mixed in near-equal proportions, HEAs present an ideal case where increased configurational entropy stabilizes solid solution phases over intermetallic phases. This entropic effect sets HEAs apart from conventional alloys, typically consisting of one or two primary constituents. Consequently, HEAs exhibit distinctive microstructural features that enhance their mechanical, thermal, and chemical performance, making them well-suited for utilisation in advanced technologies [1-3].

In the field of metallurgy, the interface between molten alloys and refractory ceramics plays a crucial role in determining the quality of cast components. Refractory ceramics, distinguished by their elevated melting points and thermal stability, pose considerable challenges when interfaced with metallic materials. The interface between refractory ceramics and metals demonstrates complex behaviours under thermal conditions, including the formation of new phases and bonding layers resulting from diffusion processes and reaction kinetics. [4,5] Various factors influence these interfacial phenomena, including material compositions, bonding

techniques, and environmental conditions. For instance, the alloying elements can either facilitate or hinder specific interactions with refractory materials, affecting microstructural evolution, phase stability, and mechanical properties [4,6]. Beyond chemical interactions, the investigation of wetting phenomena is critical. Research into wetting characteristics demonstrates that the wettability of ceramics by molten metals significantly influences their corrosion and erosion behaviour [7-10].

The present paper is focused on the experimental study of high-temperature interactions of four-element alloy with selected refractory ceramic materials. These interactions were characterized by determining wetting angles using the sessile drop technique. Temperature dependencies of density and wetting angles up to a temperature of 1600 °C were experimentally determined. The chemical and structural changes of both the alloy and the ceramic substrate were investigated using SEM and EDX analysis techniques. The findings of this research hold potential applications in metallurgy and the casting processes of high-entropy alloys.

2. EXPERIMENTAL RESEARCH

2.1 Materials

A four-element alloy was used for the experimental study of interfacial interaction with four industrial ceramic substrates. The chemical compositions of alloy and substrates before experiments are given in **Table 1** and **Table 2**, respectively.

Table 1 Chemical composition of the investigated alloy (wt%)

NiFeCoCr	Ni	Fe	Co	Cr	N	O	C	S
alloy	32.22	23.38	23.17	21.23	0.068	0.056	0.012	0.006

Table 2 Chemical composition of industrial ceramic substrates (wt%)

Substrate	Al_2O_3	SiO_2	TiO_2	Fe_2O_3	CaO	MgO	K_2O	Na_2O
1	84.72	12.94	0.29	0.69	0.17	0.14	0.41	0.18
2	73.45	24.85	0.15	0.48	0.09	0.11	0.44	0.01
3	71.71	19.05	2.51	1.98	0.39	0.36	0.60	0.09
4	68.06	25.83	2.03	2.11	0.34	0.24	0.59	0.11

2.2 Preparation of samples

Linn's Supercast Titan mid-frequency induction vacuum furnace with centrifugal casting was used to prepare the Ni-Fe-Co-Cr alloy. An annealed crucible made of Al_2O_3 was used for melting. The casting mould was made of isostatically pressed graphite. Prior to melting, the pure metals (min. 99.9 %) were mechanically and chemically cleaned. The melting process was conducted under reduced pressure, with argon 6.0 as a shielding gas. The melted system was used to cast round bars with a diameter of 20 mm and a length of 225 mm.

Small cubes with an edge length of approximately 4 mm were prepared from a given alloy. In order to remove the surface oxidic layer, each cube was mechanically polished and cleaned with acetone. The cleaned alloy cube was weighed and placed on a ceramic substrate (samples 1–4).

Ceramic plates measuring 9 mm in height were cut from cylindrical bars with a diameter of 50 mm. The upper sides of the plates were ground and polished to achieve the straightest and smoothest surface possible. Substrates were annealed at a temperature of 1150 °C for 5 hours and their surface was also cleaned with acetone, right before carrying out the experiment.

2.3 High-temperature wettability test

The experimental determination of the surface properties was conducted using the sessile drop technique. The apparatus comprised a high-temperature resistance observation furnace CLASIC and a CANON EOS 550D camera. The sample assembly was positioned in the centre of the furnace, right next to the thermocouple PtRh30%-PtRh6%, to ensure a homogeneous temperature field. The furnace was sealed, evacuated and purged with pure argon (> 99.9999 %). The furnace was then either evacuated again or filled with pure argon to a slight overpressure (110 kPa), depending on the required experimental conditions. The system was heated to a temperature of 1600 °C at a heating rate of 5 °C/min.

Images were acquired at 2 °C intervals and evaluated using axisymmetric drop shape analysis performed by in-house developed software SurfaceTension 1.0. The software performs a calibration with an image of a steel sphere of a known diameter, evaluates the dimensions of the drop, and fits the drop profile using the least squares method.

2.4 Chemical and structural analysis

The chemical and structural changes in the investigated alloy and ceramic substrates caused by mutual interactions were investigated using SEM and EDX analytical techniques. The analyses were conducted within a Quanta-650 SEM equipped with EDAX Elect Plus. The experimental conditions were the following: a voltage of 10 kV for image acquisition and 20 kV for EDX microanalysis, a beam diameter of 4–6 mm and a high vacuum. The samples were not metallically coated prior to analyses.

3. RESULTS AND DISCUSSION

The dependencies of the average wetting angles on the temperature for all ceramic substrates are shown in **Figure 1**. For each experiment, the evaluation of only a specific temperature interval was possible. The successful determination of the investigated properties is limited by the creation of an axisymmetric droplet, the acquisition of high-resolution images, and the presence of a smooth and straight substrate edge.

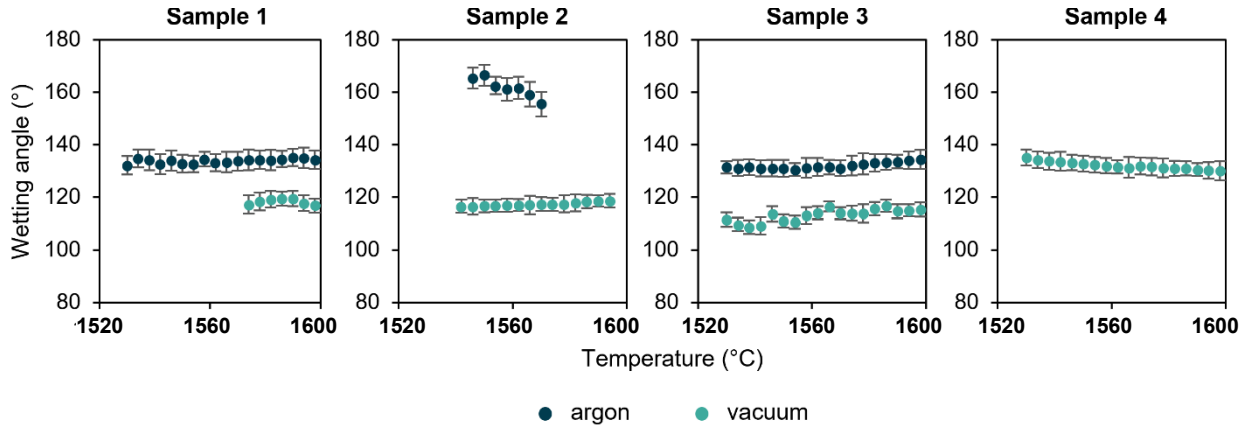

Figure 1 Comparison of the temperature dependencies of the average wetting angles (°) for samples 1–4 under both experimental conditions; error bars represent standard deviations

As displayed in **Figure 1**, all samples exhibited non-wetting behaviour. In the argon atmosphere, the values of wetting angles were found to be in the range of 130–165°. However, in a vacuum, these values were found to decrease to 109–135°. Maximum experimental scatter of 3 % from the average values was observed in all measurements. The most significant challenge of the experiment was the rapid oxidation of the alloy, which, in the case of the experiment with substrate 4 under an overpressure of argon, prevented the melting of the alloy (see **Figure 2, 4A**). Consequently, data from this experiment are not available. The images presented in **Figure 2** capture the alloy on ceramic substrates at a maximum temperature of 1600 °C.

In cases where droplet formation occurred and the interaction between the alloy and the substrate was predicted to be minimal due to the high Al_2O_3 content, the melt density was also assessed. Density decreased with increasing temperature, specifically from 7.30 to 6.86 g/cm^3 in the temperature range of 1530–1600 °C. The density was also theoretically calculated using ThermoCalc 2019a software operating with the TCFE 8 Steel/Fe-Alloy database. The calculated density decreased from 7.13 to 7.07 g/cm^3 across the same temperature range. The maximum relative error of the measured values from the calculated values was 3 %.

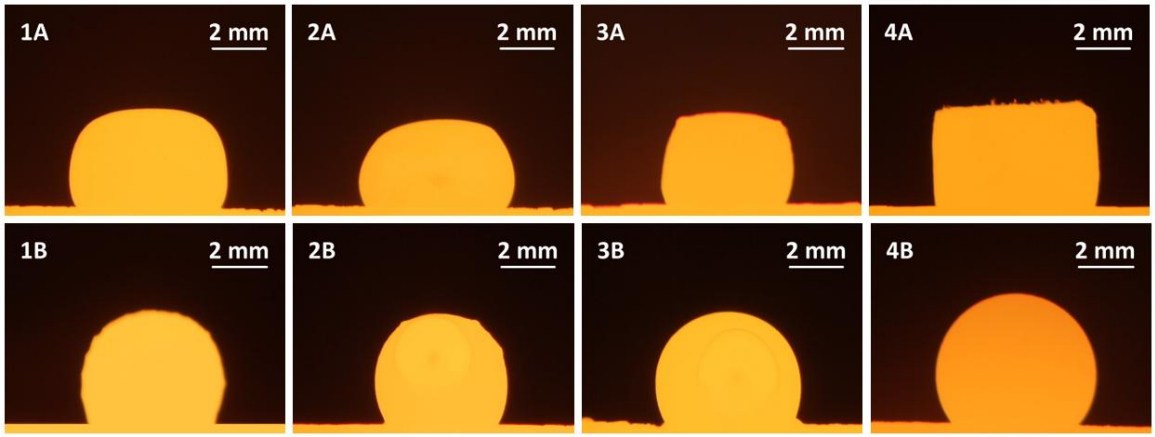

Figure 2 Images of the alloy on ceramic substrates (1–4) at T_{max} under overpressure of argon (A) and in a vacuum (B)

SEM images and EDX results are presented for substrates 1 (**Figure 3**) and 4 (**Figure 4**). For the purpose of this study, images of the substrate's wetted area, droplet underside and surface were evaluated for both experimental conditions. The detailed EDX analyses results are given in **Table 3**.

The results of the EDX analysis (**Table 3**) demonstrate that wetting of substrate 1 with the molten alloy in an argon atmosphere resulted in an increase in chromium content (1A) in the original substrate, predominantly composed of corundum (1B). Chromium substituted aluminium in the substrate surface. However, wetting the substrate in a vacuum resulted in the penetration of the alloy (4A) into the substrate's surface (4B). Due to the interaction between the substrate and the alloys, the droplet was not perfectly separated from the ceramic, and therefore pieces of substrate were also found in the images of the droplet underside. In an argon atmosphere, the substrate melted together with the alloy (2A) and created a surface composed of corundum (2C) and chromium-doped corundum (2B). The alloy (5A) penetrated the surface of substrate 1 (5B) in a vacuum, resulting in an imperfect separation. An increased content of chromium was also present on the surface of the droplet after conducting the experiment under an overpressure of argon. Chromium was found to act as a surface-active element, which, upon diffusing into the surface of the alloy, underwent oxidation (3B), forming a melt-resistant layer, which was disrupted by volume dilation of the molten alloy (3A). The surface of the droplet formed in a vacuum exhibited marked differences compared to the one formed in an argon atmosphere. Spherical iron microparticles were reduced on the droplet surface (6A), accompanied by the presence of significant amounts of aluminium and oxygen on the surface (6B).

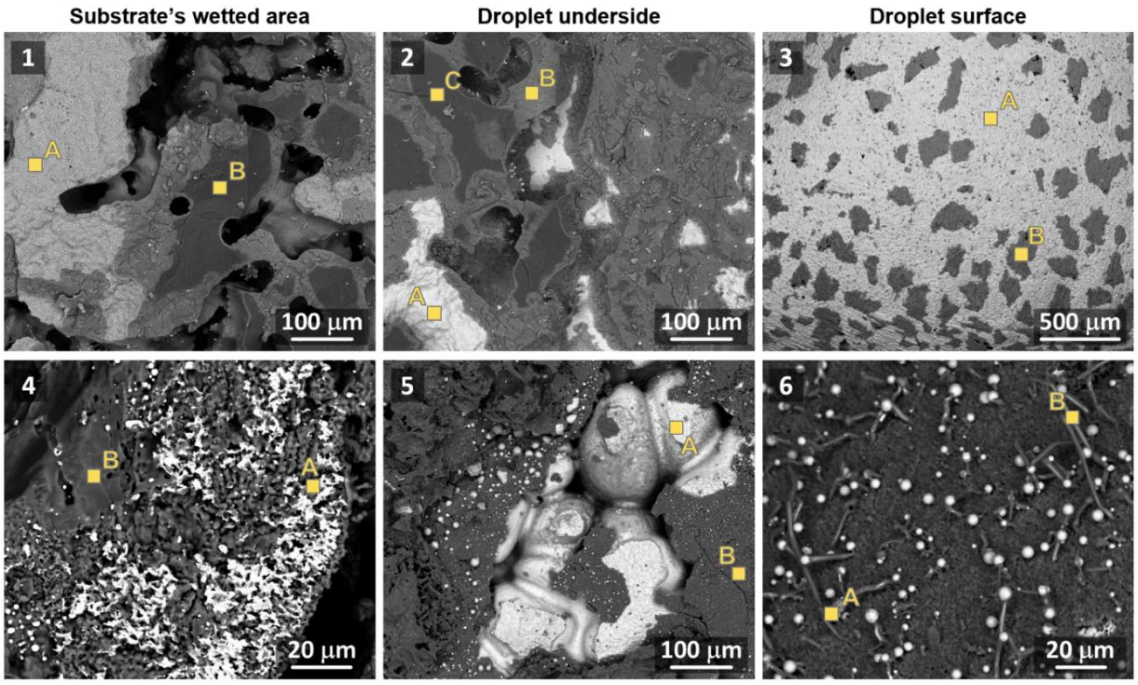

Figure 3 SEM images of the wetted area of the substrate, droplet underside, and droplet surface for sample 1 under overpressure of argon (1–3) and in a vacuum (4–6)

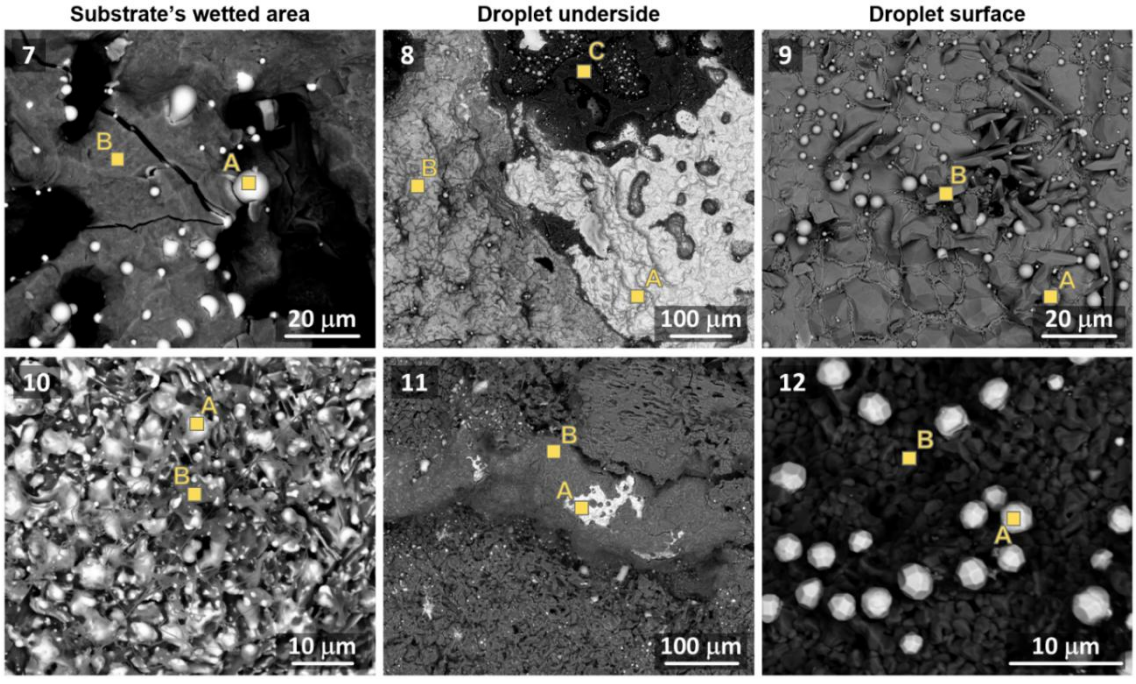

Figure 4 SEM images of the wetted area of the substrate, droplet underside, and droplet surface for sample 4 under overpressure of argon (7–9) and in a vacuum (10–12)

Compared to sample 1, the results of the EDX analysis of sample 4 revealed the presence of additional elements, as expected due to their higher quantities in the substrate (see **Table 2**). Apart from chromium-doped corundum (7B), metal microparticles (7A) were present on the surface of the substrate measured in an argon atmosphere. These particles contained a significant amount of phosphorus, which most likely underwent transformation from the phosphates present in the substrate into metal phosphides. Similarly to

sample 1, the substrate was melted together with the alloy melt (8A), creating a surface containing pieces of substrate more (8B) or less (8C) enriched with alloy metals. Chromium accumulation and oxidation (9B) occurred again on the droplet surface, accompanied by the presence of microparticles of metal phosphides (9A). Regarding the measurements in vacuum, a coating consisting of phosphides of iron and a smaller proportion of titanium (9A) was formed on the surface of the substrate (9B). The substrate was penetrated by the alloy, rather than being melted together with it. Consequently, the droplet underside consisted of two phases: the alloy (11A) was found to be adhered to pieces of the substrate (11B). The droplet surface contained a significant amount of aluminium and oxygen, with traces of chromium, iron, and cobalt (12B). The present microparticles were found to be predominantly composed of iron, chromium, and silicon (12A).

Table 3 EDX analyses results (at%) for highlighted points from **Figure 3** and **Figure 4**; numbers 1–12 represent the image and letters A–C represent the analysed point

Point	O	Al	Si	Cr	Fe	Co	Ni	P	Ti	Mg	Ca
1A	55.08	12.44		32.48							
1B	49.43	50.57									
2A	6.39	2.61	1.37	20.74	21.75	19.98	27.15				
2B	56.95	31.58	1.37	10.10							
2C	50.10	49.90									
3A	2.49			22.65	23.57	22.02	29.27				
3B	58.03	2.80		39.17							
4A	14.09	15.00		12.63	20.61	18.87	18.80				
4B	52.34	47.66									
5A	2.94	11.79		18.47	24.69	21.16	20.95				
5B	57.80	39.93		1.22	1.05						
6A	24.61	7.46		2.40	65.54						
6B	45.95	54.05									
7A	17.00	5.08		3.26	50.50	3.85	5.01	15.29			
7B	56.27	26.82	0.94	15.98							
8A	16.96	1.88		17.72	20.41	18.57	24.46				
8B	40.26	5.91	1.52	19.86	10.51	9.44	12.50				
8C	51.90	18.73	23.34	6.04							
9A	10.49			6.26	24.35	19.18	28.50	11.23			
9B	62.76			37.24							
10A	15.41	2.95	1.17		61.59			17.08	1.79		
10B	47.95	46.39							1.14	1.18	3.33
11A	11.81	12.10	1.19	34.16	25.52	9.57	5.64				
11B	56.36	40.17	2.88						0.26		0.33
12A	14.59	10.50	29.03	12.07	33.80						
12B	47.60	44.32		4.77	2.45	0.86					

4. CONCLUSIONS

The following conclusions were drawn from the data obtained:

- all the samples exhibited non-wetting behaviour, the wetting angle values were determined to be in the range of 130–165° for an argon atmosphere and 109–135° for a vacuum,
- the maximum relative error observed in the measured density values in comparison to the calculated density values was 3 %,
- under overpressure of argon, the surface of the metal droplet was substantially oxidized, and inter-melting with the substrate occurred,
- in a vacuum, a significant amount of metal microparticles were found on the droplet surface, part of the alloy also penetrated the substrate,
- for the substrate with lower corundum content, metal phosphides were present on the substrate or droplet surface in the form of spherical microparticles.

Further investigation including complementary analyses is needed for the right interpretation of the mechanism of mentioned interactions. This work is the first step of our research focused on interaction of high-entropy alloys with industrial refractory ceramic materials, and it will be supplemented with further findings in the near future.

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Data Availability Statement: The original data presented in the study are available in ZENODO at https://10.5281/zenodo.15410839, accessed on 14 May 2025.

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