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High-temperature protective coatings and methods of their analysis

Wysokotemperaturowe powłoki ochronne i metody ich analizy

Materials used for elements of the hot part of aircraft engines must fulfill a number of requirements, including high temperature corrosion resistance, durability and good strength in a wide temperature range. The continuous increase in engines' efficiency by increasing their operating temperature resulted in the need to use heat-resistant protective coatings. Currently, aluminum layers or multi-component MCrAlY alloys are used. However, the use of an alternative fuel in the form of hydrogen means that the coatings must be resistant to water vapor at high temperatures. Hence, the work proposes high entropy alloys (HEA) as a candidate for materials for protective coatings. At the same time, basic methods for analyzing high-temperature corrosion products on the mentioned protective coatings are presented.

Keywords: corrosion, high temperature corrosion resistant coatings, analytical methods

Materiały stosowane na elementy gorącej części silników lotniczych muszą spełniać wiele wymagań, przede wszystkim musi je cechować wysoka żaroodporność, trwałość, jak również dobra wytrzymałość w szerokim zakresie temperatury. Ciągłe zwiększanie sprawności silników poprzez podnoszenie temperatury ich pracy spowodowało, że konieczne stało się stosowanie żaroodpornych powłok ochronnych. Obecnie stosuje się warstwy aluminiowe lub wieloskładnikowe stopy typu MCrAlY. Używanie wodoru jako paliwa alternatywnego sprawia, że powłoki muszą być odporne na działanie pary wodnej w wysokiej temperaturze. W pracy zaproponowano stopy o wysokiej entropii mieszania (HEA) jako potencjalne materiały na powłoki ochronne. Przedstawiono także podstawowe metody analizy produktów korozji wysokotemperaturowej na takich powłokach.

Słowa kluczowe: korozja, powłoki żaroodporne, metody analityczne

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1. Introduction

Metallic materials are now the most widely used group of materials in almost every area of our lives. Compared to ceramic and polymeric materials, metallic materials have good electrical and thermal conductivity, as well as good mechanical properties such as high strength and hardness [1]. Materials used in turbojet engines or in stationary gas turbines, such as nickel superalloys, are exposed to temperatures in the 900–1200°C range and to aggressive gases, such as oxygen, carbon dioxide or sulfur dioxide, and exhaust gases. The metal alloys used for structural components designed for elevated-temperature operation are mainly alloy steels and nickel superalloys. The use of nickel superalloys began as early as the 1940s. Initially, nickel matrix alloys were used for metal forming (years around 1940–1970), which have operating temperatures in the range of 800–900°C. Another type of nickel alloy included vacuum-cast alloys (1960–1980), which could be used at temperatures up to about 1000°C. In 1970, directional crystallization technologies were introduced, for which the maximum operating temperature was 1050°C. However, the breakthrough came with the introduction of technologies for producing monocrystalline nickel superalloys, for which the operating temperature reaches 1100°C (Fig. 1) [2].

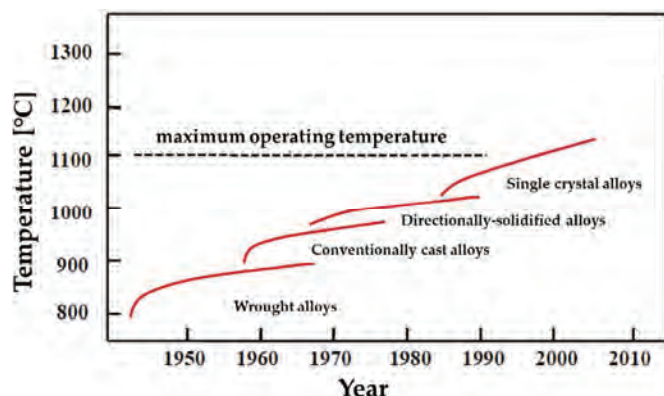


Fig. 1. Schematic illustration of development of high temperature alloys and their application
Source: [2, p. 19].

Rys. 1. Schemat rozwoju stopów wysokotemperaturowych oraz temperatury ich stosowania
Źródło: [2, s. 19].

These materials, operating in high temperature conditions and oxidizing gas atmospheres, degrade [3]. This process leads to undesirable turbojet engine downtime, the need for repairs, and in extreme cases to incidents and aircraft accidents. At the same time, for various reasons, both economic (reducing the frequency of engine repairs) and environmental (reducing exhaust emissions), there is a constant effort to increase the efficiency of turbojet engines. One of the simplest ways to do this is to increase the temperature at the inlet of the high-pressure turbine, which follows the Carnot cycle [4]. Increasing engine efficiency is associated with reduced fuel consumption and, therefore, with reduced exhaust emissions per km of travel. One consequence of increasing engine operating temperature is also an acceleration of the degradation of metallic materials currently used in the hot part of aircraft engines. In order to increase heat resistance, high-temperature pro-

tective coatings are produced on structural components made of nickel superalloys. These coatings can be aluminide layers [5, 6] or MCrAlY-type alloy coatings [7, 8]. These layers are characterized by high resistance to high-temperature corrosion due to their ability to form a protective Al_2O_3 oxide scale. The production of aluminide layers leads to the formation of a β -NiAl phase, which is a reservoir of Al necessary for the formation of protective Al_2O_3 scale over the long life of the components. Aluminide layers are produced by chemical reaction in aluminizing processes. These processes can be divided based on Al activity into low temperature high activity (LTHA) and high temperature low activity (HTLA) processes. The main aluminizing processes in the LTHA group are the contact-gas ("in-pack-cementation"), non-contact-gas ("out-of-pack cementation") and immersion ("slurry aluminizing") methods. In addition, attention is focused on reducing greenhouse gas emissions into the atmosphere. Hence, there is a strong trend away from fossil fuels toward alternative fuels, such as hydrogen-enriched fuels [9]. However, hydrogen combustion, in addition to reducing atmospheric greenhouse gas emissions, comes with certain consequences. First, hydrogen combustion increases the temperature of the exhaust gas and thus the operating temperature of the materials used in the hot parts of turbines. Second, hydrogen combustion increases the water vapor content of the exhaust gas. The increased combustion temperature practically eliminates nickel superalloys from their use, since for the time being their operating temperature has reached the maximum temperature limit for their use, which is up to about 1100°C. In addition, the high concentration of water vapor in the operating atmosphere of metallic materials adversely affects their heat resistance [10–13]. Therefore, solutions are being sought to ensure the possibility of using metal alloys that can potentially replace the nickel superalloys used under the conditions described above. Increasing the concentration of water vapor in the flue gas due to the combustion of hydrogen fuels poses a significant challenge for materials engineering. As shown in numerous publications, the degradation of both metal alloys and coatings in an atmosphere containing water vapor is significantly accelerated [14, 15], so there is a need to find new material solutions with increased resistance to high-temperature water vapor. High entropy alloys (HEA) are a group of new materials characterized by excellent mechanical properties [16] and enhanced resistance to high-temperature corrosion [17].

2. Experimental

A complete characterization of the high-entropy protective coatings can be obtained through a comprehensive analysis of the phase composition: by X-ray diffraction (XRD) methods, microstructure and chemical composition: by optical microscopy (LOM), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) methods, and heat resistance tests in various corrosive atmospheres. In this paper, the produced heat-resistant layers and coatings, as well as the chemical composition and microstructure of the produced high entropy mixing alloys, were characterized using a HITACHI S-3400N scanning electron microscope. However, the analysis of chemical composition by scanning electron microscopy using an EDS detector has some limitations due to the nature of the method. Namely, elements with a low atomic number are difficult to analyze due to the low number of electrons that can be excited. Hence, a method that

perfectly complements the analysis of the chemical composition of protective coatings, as well as corrosion products, is the glow discharge optical emission spectrometry (GD-OES) method. The essence of the method is the generation of a plasma from high purity argon (6N), the acceleration of argon ions toward the surface of the test sample, and the collision of the accelerated ions with the surface of the test sample. As a result of the collision, atoms of elements are knocked off the surface of the sample, which in turn, entering the plasma, undergo first excitation and then recombination. During recombination, excess energy is emitted from the excited atom in the form of a quantum of light radiation of a well-defined wavelength. This light is redirected to a polychromator, and then the intensity of the light radiation for a specific element is analyzed and monitored as a function of measurement time using detectors. As the atoms of the surface of the sample are evaporated, the measurement time can be correlated with the distance from the surface of the sample in depth. A significant advantage of the GD-OES method is the ability to measure 64 elements simultaneously and its sensitivity for both low and high atomic number elements, as well as its resolution, which can analyze coatings with thicknesses ranging from nanometers to about 120 μm . The advantages of the method also include the relatively fast measurement time: analysis to maximum depth takes about 3,600 seconds. The result of the analysis is a graph of the relationship of the intensity of light wave emission by individual elements as a function of time. It is also possible to convert the results obtained to graphs of the concentration of a given element as a function of time, or as a function of depth using so-called RSF (relative sensitivity factors) [18–20]. Despite its several advantages, the method has limitations. One of them is the overestimation of the oxide concentration in the substrate material. After the quantification process, it equals approximately 1 at%. A pre-vacuum of 10^{-3} Pa is generated in the chamber where the plasma is formed. This causes the chamber to contain oxygen contamination, which affects the final oxygen concentration in the GD-OES profile. However, this limitation is widely accepted. The chemical composition of the produced coatings was analyzed using a GD Profiler HR plasma discharge optical emission spectrometer.

A heat resistance test of high entropy mixing alloys was carried out at 1000°C for up to 1000 h in two atmospheres: air using a Nabertherm SN 313602 chamber furnace and air with 20% water vapor by volume using a MagmaTherm tube furnace. A RADWAG WAA 100/C/1 microscale with an accuracy of 0.1 mg was used to measure mass change.

3. Research material

In this study, the following heat-resistant layers and coatings were characterized:

- aluminide layers produced by the contact-gas method,
- aluminide layers produced by the chemical vapor deposition method,
- MCrAlY-type coatings by the low-pressure plasma spraying (LPPS) method.

A mixture of powders was used to produce aluminide layers by the contact-gas method on a Hastelloy-X superalloy substrate: 15 wt% Al, 3 wt% NH_4Cl and 82 wt% Al_2O_3 filler. The process was carried out at

650°C for 6 h in a Carbolite STF 16/450 furnace in an Ar atmosphere of 5N purity.

Aluminide layers on the Hastelloy-X superalloy substrate were produced by Chemical Vapor Deposition (CVD) using a Bernex BPX Pro 325 S CVD device. The aluminization process was carried out at 1040°C for 6 h in an atmosphere of AlCl_3 and H_2 mixture. Heat-resistant coatings of the MCrAlY type were produced by low pressure thermal spraying (LPPS) using the MultiCoat® LPPS® device.

High entropy alloys with equal concentrations of Co, Ni, Al, Cr and Fe were doped with Mo in concentrations in the range of 1–5 at%. The alloys were produced from high-purity powders (min. 99.999%) by pressing their mixtures and melting them five times in an ARC-Melter arc furnace. Table 1 shows the nominal chemical composition of high entropy alloys for coating materials with enhanced heat resistance in a steam atmosphere.

Table 1. Nominal chemical composition of investigated high entropy alloys (HEA) expressed in at%

Tabela 1. Nominalny skład chemiczny badanych stopów wysokiej entropii mieszania (HEA) wyrażony w at%

Name of the alloy	Element [at%]					
	Co	Ni	Al	Cr	Fe	Mo
REF	20.00	20.00	20.00	20.00	20.00	0.00
REF + 1Mo	19.80	19.80	19.80	19.80	19.80	1.00
REF + 2Mo	19.60	19.60	19.60	19.60	19.60	2.00
REF + 3Mo	19.40	19.40	19.40	19.40	19.40	3.00
REF + 4Mo	19.20	19.20	19.20	19.20	19.20	4.00
REF + 5Mo	19.00	19.00	19.00	19.00	19.00	5.00

4. Analysis of test results

A typical microstructure of an aluminide layer produced by the LTHA process is shown in Fig. 2a. On the other hand, the aluminide layers can be produced by the HTLA is chemical vapor deposition (CVD). In this method reactants, most often Al halides, are transported in the gas phase to a retort (reaction chamber), in which, due to a chemical reaction, a β -NiAl layer is produced. A typical microstructure of an aluminide layer produced by CVD is shown in Fig. 2b. In both cases, the microstructure is characterized by the presence of three zones: the β -NiAl aluminide layer, the diffusion zone and the substrate material.

Heat-resistant coatings of the MCrAlY type are produced by thermal spraying processes. These processes can be air plasma spraying (APS), low pressure plasma spraying (LPPS) and vacuum plasma spraying (VPS). A typical microstructure of MCrAlY-type coatings is shown in Fig. 3.

An example coating and its elemental distribution is shown in Fig. 4: Fig. 4a reveals the microstructure of the analyzed protective coating (aluminide layer), Fig. 4b shows a graph illustrating the relationship between intensity and time of measurement, while Fig. 4c reveals the GD-OES profile quantified using RSF coefficients showing a graph of elemental concentration as a function of measurement time. The results clearly indicate the high utility of the method in the analysis of protective layers and coatings.

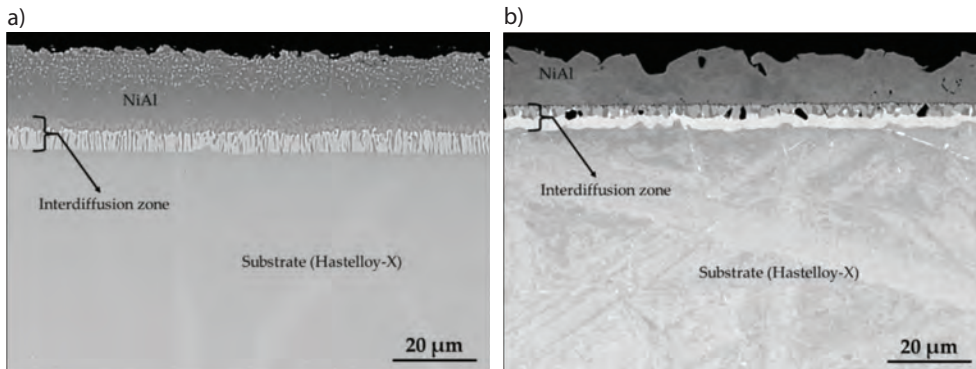


Fig. 2. Microstructure of an NiAluminide layer formed on Hastelloy X during: a) "in-pack cementation method", 650°C, 6 h – LTHA, b) CVD, 1040°C, 6 h – HTLA
Rys. 2. Mikrostruktura warstwy aluminidkowej NiAl wytworzonej na podłożu nadstopu Hastelloy-X metodą: a) „in-pack cementation”, 650°C, 6 h – LTHA, b) CVD, 1040°C, 6 h – HTLA

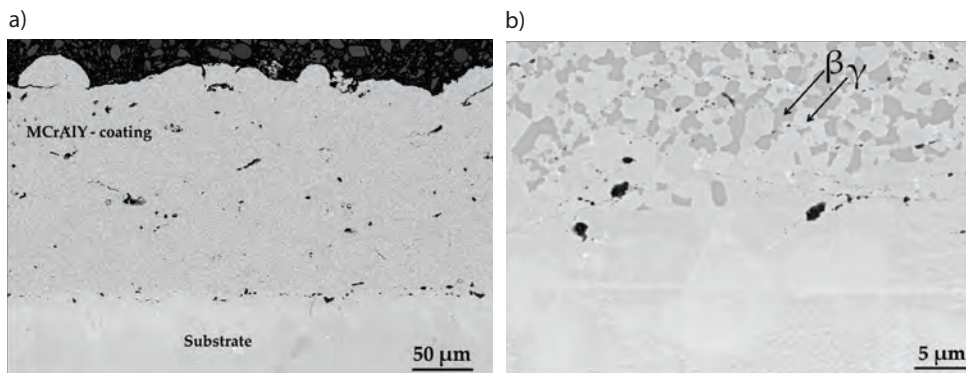


Fig. 3. Microstructure of MCrAlY thermal sprayed coating on PWA 1483 superalloy substrate: a) general view, b) detailed view showing the presence of γ -Ni solid solution phases and β -NiAl intermetallic phase

Rys. 3. Mikrostruktura powłoki typu MCrAlY natryskiwana cieplnie na podłożu nadstopu PWA 1483: a) widok ogólny, b) widok szczegółowy, ukazujący obecność faz roztworu stałego γ -Ni oraz fazy międzymetalicznej β -NiAl

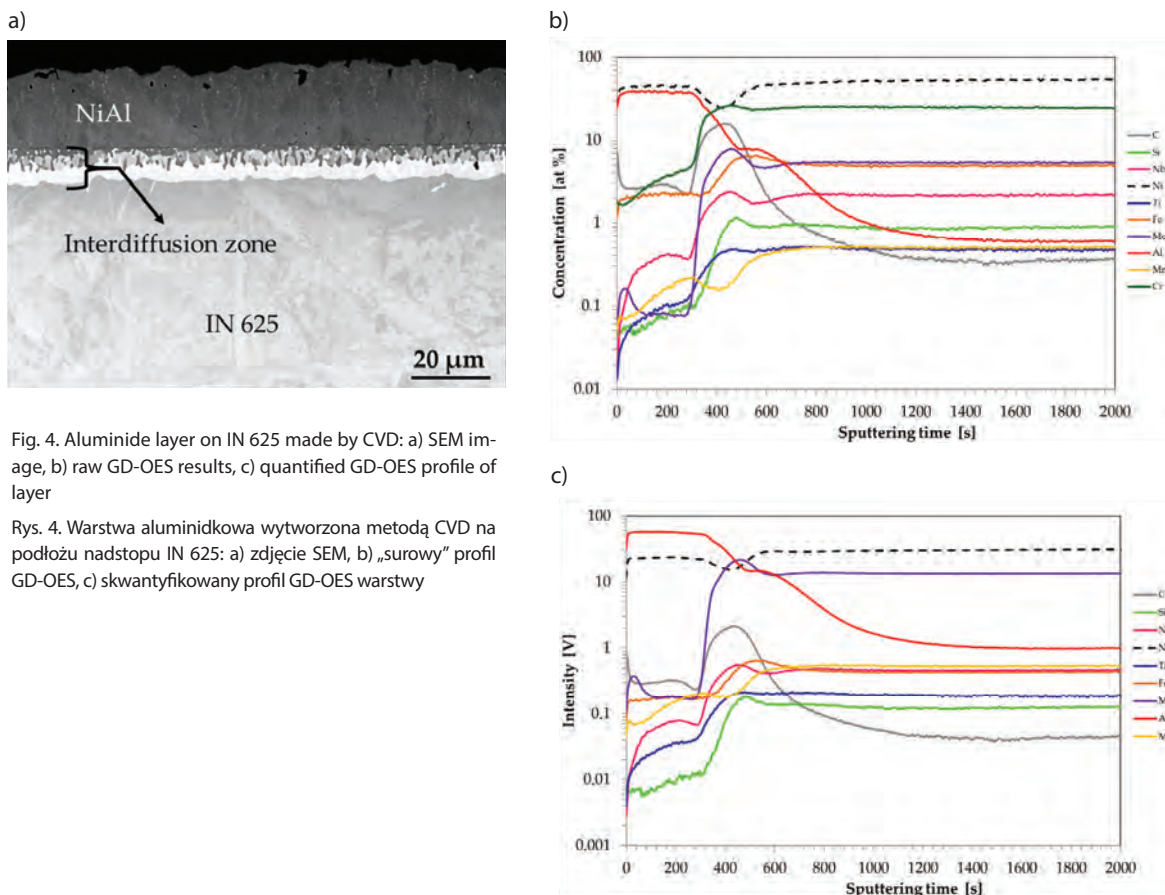


Fig. 4. Aluminide layer on IN 625 made by CVD: a) SEM image, b) raw GD-OES results, c) quantified GD-OES profile of layer

Rys. 4. Warstwa aluminidkowa wytworzona metodą CVD na podłożu nadstopu IN 625: a) zdjęcie SEM, b) „surowy” profil GD-OES, c) skwantyfikowany profil GD-OES warstwy

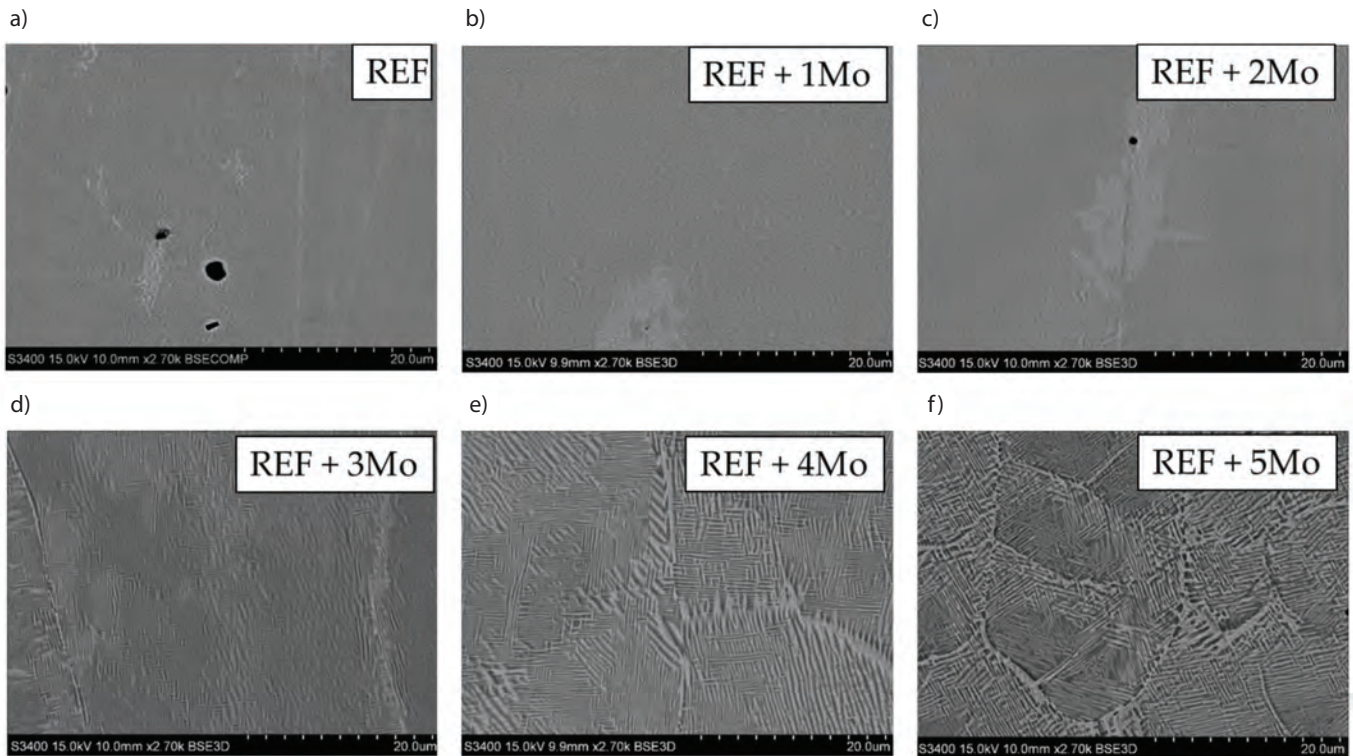


Fig. 5. Microstructure of studied Co, Ni, Al, Cr i Fe + xMo HEA in the as-cast conditions: a) 0Mo, b) 1Mo, c) 2Mo, d) 3Mo, e) 4Mo, f) 5Mo
 Rys. 5. Mikrostruktura stopów wysokiej entropii mieszania Co, Ni, Al, Cr i Fe + xMo w stanie lany: a) 0Mo, b) 1Mo, c) 2Mo, d) 3Mo, e) 4Mo, f) 5Mo

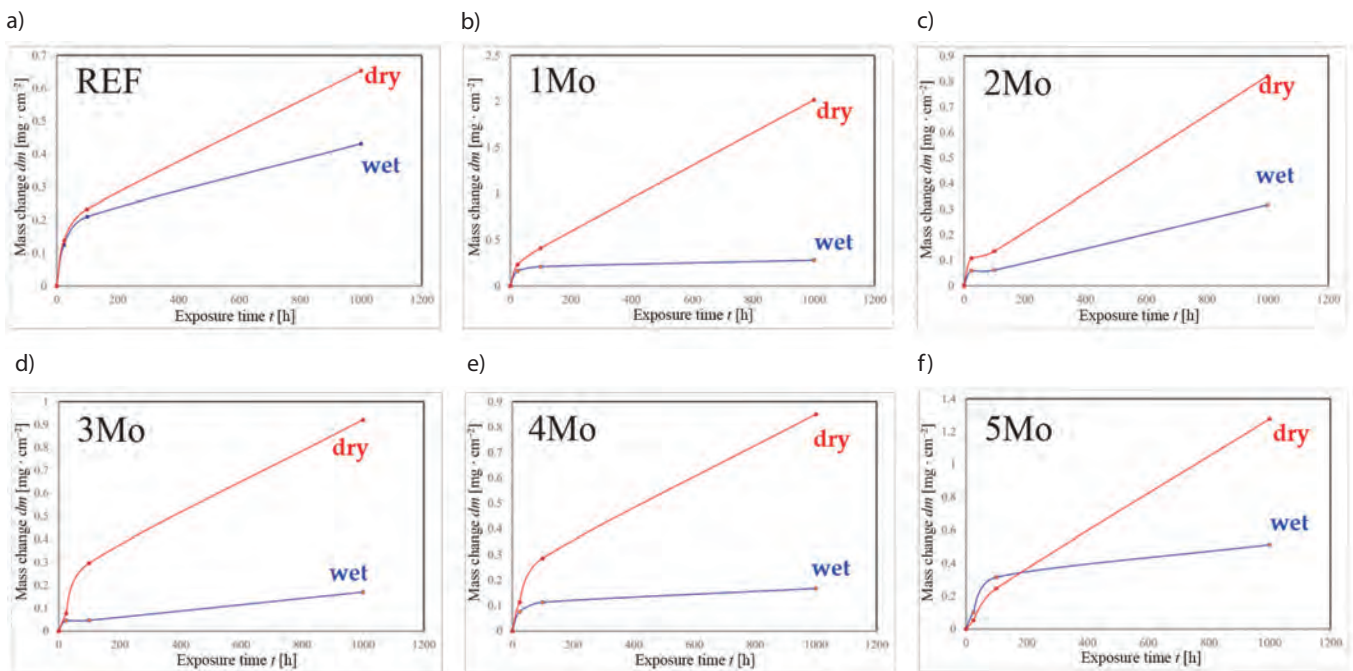


Fig. 6. Mass change plots of studied HEA exposed at 1000°C up to 1000 h in dry and wet atmospheres: a) 0Mo, b) 1Mo, c) 2Mo, d) 3Mo, e) 4Mo, f) 5Mo
 Rys. 6. Zmiany masy badanych stopów wysokiej entropii mieszania podczas próby utleniania wysokotemperaturowego w temperaturze 1000°C w czasie do 1000 h w atmosferze suchej i mokrej: a) 0Mo, b) 1Mo, c) 2Mo, d) 3Mo, e) 4Mo, f) 5Mo

For the studied high entropy mixing alloys, changes were observed in the microstructure of the produced alloys depending on the concentration of the alloying element (Mo; Fig. 5). The formation of an increasingly ordered, mosaic microstructure of the alloys was found as the molybdenum concentration increased. This

mosaic microstructure was identified as a Widmanstätten structure [21]. The results of the oxidation kinetics study are presented in Fig. 6. Lower oxidation kinetics were observed for samples oxidized in a steam-containing atmosphere compared to a dry atmosphere regardless of alloying element concentration. The obtained

results indicate that the studied high entropy mixing alloys are excellent candidates for protective coating materials operating in hydrogen fuel exhaust atmospheres.

5. Conclusion

Based on the results reported in this paper, it was observed that:

- Aluminide layers and MCrAlY-type coatings improve the heat resistance of aircraft engine components by forming a protective Al_2O_3 scale and becoming an Al reservoir.
- Introduction of hydrogen fuel results in an increase in the concentration of water vapor in the flue gas, which in turn negatively affects the heat resistance of alloys and layers.
- Preliminary results on HEA in a vapor atmosphere showed their enhanced heat resistance compared to a dry atmosphere, indicating that these alloys have high application potential for protective layers of hydrogen fuel engine components.
- Analysis of coatings through the study of heat resistance, microstructure (optical, scanning and transmission microscopy), phase composition (XRD) and chemical composition (particularly GD-OES) allows a full and comprehensive characterization of protective coatings used in aircraft engines.
- The GD-OES method is an excellent complement to standard methods of chemical composition analysis.

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CRedit authorship contribution statement

Wojciech J. Nowak: Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Methodology, Project administration, Resources, Supervision, Validation, Visualization, Writing – original draft, Writing – review & editing.

Urszula Paszek: Conceptualization, Validation, Visualization, Writing – original draft, Writing – review & editing.

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