Development of Wear-Resistant High-Entropy Alloy Coatings Produced by Thermal Spray Technology

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Development of wear-resistant high-entropy alloy coatings produced by thermal spray technology

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The alloying concept of High-Entropy Alloys (HEA) has attracted much scientific interest due to an interesting combination of properties. Previous investigations have shown that high hardness and strength, comparable to bulk metallic glasses, can be achieved. Furthermore, HEAs show distinct ductility and good high-temperature resistance. First investigations on tribological properties are indicating high wear resistance. Previous investigations of the alloy system AlCoCrFeNiTi in bulk state have shown promising properties. Therefore, the alloy AlCoCrFeNiTi with equimolar composition was selected for transferring bulk properties to thermally sprayed coatings. The focus of this contribution is on studying tribological properties of thermally sprayed HEA coatings to enlarge the field of possible applications.
Feedstock material production was carried out by high-energy ball milling (HEM) and inert gas atomization. Subsequently, coatings were deposited by Atmospheric Plasma Spray (APS). Tribological properties of the coatings under different wear regimes were investigated in ball-on-disk wear tests, oscillating wear tests and scratch tests. The tribological properties are compared with a conventional hard chrome plating and correlated with microstructure.

1 Introduction

The concept of HEA was introduced by J.W. Yeh et al. [1]. This new concept comprises an alloy composition with at least 5 elements each with a share of 5 – 35 at.%. Investigations have shown the formation of simple solid solutions with face centered cubic (FCC) and body centered cubic (BCC) structures due to the stabilization by high entropy effect. Contrary to first expectations, no brittle, intermetallic or complex phases were formed [1-2]. Independent investigations by Cantor et al. revealed a single phase face centered cubic structure in the equimolar alloy FeCrMnNiCo [3]. Further investigations of HEAs showed the formation of a multiphase structure consisting of several phases for most alloy system. For alloys which do not consist of one simple solid solution, the term compositionally complex alloys (CCA) was introduced [4].
In this paper, the equimolar alloy AlCoCrFeNiTi is investigated. Microstructural studies of the alloy system showed a dendritic structure with two BCC solid solutions [5]. Mechanical investigations in compression tests revealed promising properties, including a high fracture strength of 2.58 GPa and plastic strain of 8.8 %. In this particular alloy system, these properties were attributed to solid solution strengthening by large Ti atoms [5]. The focus of subsequent studies were microstructure and mechanical properties. Two alloying elements showed strong influence on alloy properties: Titanium and Aluminium. Aluminium is a promoter of BCC phases. For alloys with high Al content, mainly strong and brittle BCC phase are formed. Adding large Titanium atoms causes strengthening by solid solution hardening. But for alloys with high amounts, intermetallic precipitates were formed, causing embrittlement [5, 6].
First investigations on tribological properties of the CCA system AlCoCrFeNiTi showed good wear resistance, also in comparison with conventional steel (SUJ2, SKH51), which makes it promising for further investigations [7].
The wear resistance of thermally sprayed HEAs and CCAs have only been briefly studied yet [8].
The aim of this study is to apply the alloy AlCoCrFeNiTi for surface engineering to produce wear resistant coatings.

2 Experiments

In this study, the alloy AlCoCrFeNiTi with equimolar composition is investigated. Two different feedstock material production routes are investigated. The first approach to produce thermal spray feedstock was the application of high-energy ball milling (HEM). In a first step, a powder blend was produced. Therefore, pure elemental powders were utilized, except Fe. Fe was added as pre-alloy FeCr13. Cyclic milling was carried out in a Zoz Simoloyer CM08 mill with a rotor speed of 400-700 rpm and a powder mass of 0.8 kg. 8 kg of steel balls (100Cr6) with a diameter of 5 mm were used as grinding medium. Stearic acid was added as a process control agent. The process was carried out under air.
Another approach for the production of thermal spray feedstock was inert gas atomization, where Argon

was used as a process gas. The particle fraction with D_{90}< 100 µm was used for thermal spray.

Both feedstock materials were investigated regarding their powder size distribution by Laser diffraction analysis (Cilas 930). Furthermore, metallographic cross sections were prepared and investigated in Scanning Electron Microscope / SEM (Leo 1455VP) equipped with a backscattered electron detector (BSD) to examine the structure, homogeneity and particle morphology. The chemical composition was investigated by energy dispersive X-Ray spectroscopy / EDX (EDAX Genesis) and phase analysis was conducted by X-Ray diffraction / XRD (D8 Discover / Bruker AXS) using Co-K_{α}-radiation.

Before coating, steel flat substrates (S235) were prepared by corundum blasting (grain size: 425-600 µm; pressure: 3.5 bar; distance: 100 mm; angle: 60°). The coating process was carried out with the APS system GTV F6, applying the parameters displayed in Table 1.

Table 1. APS parameters.

	HEM powder	atomized powder
Ar	38 l/min	54 l/min
H_2	12.5 l/min	9 l/min
I	600 A	530 A
spray distance	120 mm	120 mm
speed	70 m/min	100 m/min
offset	4 mm	4 mm

The microstructure and phase composition of the coatings was investigated by analyzing cross sections in SEM (BSD). Furthermore, the chemical composition was determined by EDX. Wear behavior under different tribological conditions was tested in ball-on-disk (Tetra Basalt Tester), oscillating wear (Wazau SVT 40) and scratch tests (CSM Revetest-RST). The parameters are shown in Table 2.

Table 2. Wear test parameters.

ball-on-disk test		***oscillating wear test***		***scratch test***	
force	20 N	**force**	26 N	**force**	1-200 N
radius	5 mm	**frequency**	40 Hz	**speed**	2.5 mm/min
speed	96 rpm	**time**	900 s	**length**	5 mm
cycles	15916	**amplitude**	0.5 mm	**tip**	Truncated diamond Cone r: 200 µm
Ø Al_2O_3	6 mm	**Ø Al_2O_3**	10 mm		

Resulting wear marks were investigated with the Laser Scanning Microscope (LSM) Keyence VK-X200.

3 Results and Discussions

Feedstock material particle size distribution was investigated by laser diffraction analysis. For HEM feedstock material, the analysis was not possible due to the irregular particle shape. For the atomized powder, a d_{50} value of 42.9 µm and a d_{90} value of 109.9 µm was revealed. Phase analysis by XRD was carried out for both feedstock materials. Resulting diffractograms are displayed in Fig. 1.

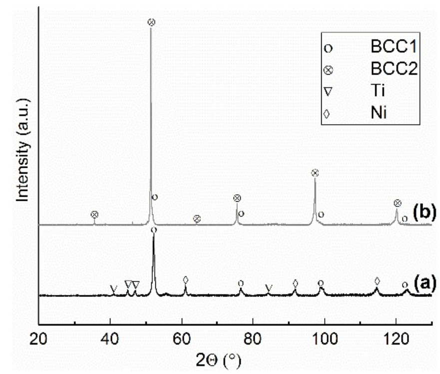

Fig 1. XRD diffractograms of (a) HEM and (b) atomized powder feedstock.

Peaks of elemental Ti and Ni can be seen in the diffraction pattern of the HEM powder, showing that no homogeneous and fully alloyed powder was obtained with this production method. Furthermore peaks appear which can be referred to a BCC phase (BCC1). The diffraction pattern of the atomized powder exhibits high intensity peaks, which can be attributed to another BBC phase (BCC2). Diffraction patterns also match with the BCC1 phase.

Metallographic cross sections of both feedstock materials are displayed in Fig. 2.

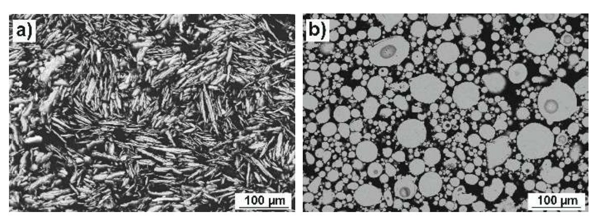

Fig 2. Cross-sections of (a) HEM powder and (b) atomized powder feedstock.

In the cross-section of the HEM powder, plate-like and heterogeneous particles can be seen. The atomized powder consists of more spherical and homogeneous particles.

The chemical composition of both feedstock materials was investigated by EDX. Results are shown in Table 3.

Table 3. Chemical composition of feedstock material.

	Al [at.%]	Co [at.%]	Cr [at.%]	Fe [at.%]	Ni [at.%]	Ti [at.%]
Nominal	*16.7*	*16.7*	*16.7*	*16.7*	*16.7*	*16.7*
HEM powder	24.3	19.8	15.7	13.7	13.8	12.7
atomized powder	18.3	16.0	16.9	16.7	16.1	16.0

For the HEM powder, a distinct deviation between measured and nominal chemical composition exists. In contrast, the atomized powder is in good accordance with the nominal composition.

After the coating process, phase analysis of the resulting coatings was carried out by XRD. The resulting diffractograms are shown in Fig. 3.

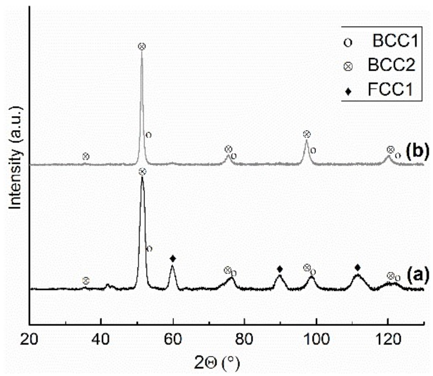

Fig 3. XRD patterns of coatings produced with a) HEM and b) atomized powder feedstock.

For the coatings deposited with HEM powder, feedstock diffraction peaks appear, which can be attributed to two BCC phases. These phases are identical to the phases BCC1 and BCC2 in the feedstock material. In contrast to the HEM powder feedstock, no peaks of elemental Ti and Ni appear. Therefore a FCC phase is formed. The diffraction pattern of the coating produced with atomized powder feedstock shows the same peaks like the feedstock material, comprising two BCC phases.

Subsequently, the coating microstructure was investigated in SEM. Cross- sections of the coatings are displayed in Fig. 4.

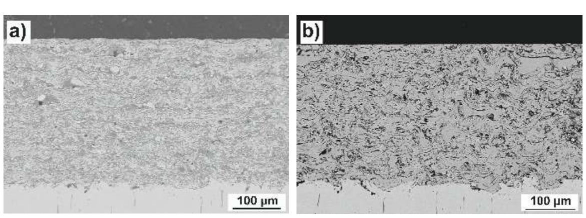

Fig. 4. SEM (BSD) images of coating cross sections produced with a) HEM and b) atomized powder feedstock.

The coating produced with HEM powder feedstock exhibits an inhomogeneous microstructure. Distinct contrast between different phase areas can be seen with BSD contrast, indicating strong differences in chemical compositions of the phase areas. In the cross section of the coating produced with atomized powder feedstock, no distinct contrast between single phase areas is observed, indicating a more homogeneous state. However, black oxide lamella and pores also exist.

The chemical composition of both coatings has been investigated by EDX and is shown in Table 4.

Table 4. Chemical composition of APS coatings produced with HEM and atomized powder feedstock.

	Al [at.%]	Co [at.%]	Cr [at.%]	Fe [at.%]	Ni [at.%]	Ti [at.%]
Nominal	*16.7*	*16.7*	*16.7*	*16.7*	*16.7*	*16.7*
HEM Powder	16.1	16.9	11.2	16.1	16.9	22.8
Atomized powder	18.7	16.3	15.2	16.3	16.5	17.0

The chemical composition of the coating produced with HEM powder feedstock distinctly deviates from the nominal composition, especially the Cr and Ti content. Furthermore, the chemical composition is also markedly changed in comparison to the feedstock material due to vaporization during the coating process. In contrast, the chemical composition of the coating produced with atomized powder feedstock is in better accordance with nominal composition. Vaporization of single elements has been reduced by a more homogeneous state of the feedstock material.

After microstructural investigations, the wear behaviour under different tribological conditions was studied. Results are displayed in Fig 5.

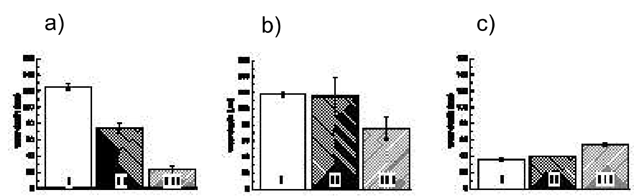

Fig 5. Wear test results of a) ball-on-disk b) oscillating wear and c) scratch test of hard chrome plating (I) and coatings produced with HEM (II) and atomized powder feedstock (III).

For the reference hard chrome plating, the highest wear depth was measured in ball-on-disk test. By applying thermal spray with CCAs, a reduction of wear depth can be achieved. For the coating produced with atomized powder feedstock, the lowest wear depth and highest wear resistance was measured.

Oscillating wear test results reveal similar wear depth for hard chrome plating and APS coating produced with HEM powder feedstock. However the coating produced with HEM powder feedstock exhibits a high standard deviation, which is caused by the inhomogeneous state of the coating. In contrast, the wear depth could be distinctly reduced by applying atomized powder feedstock due to the more homogeneous microstructure and the absence of soft FCC phase.
Results of the scratch test reveal the lowest wear depth for the hard chrome plating. Higher wear depths were measured for both APS coatings. The highest wear depth was measured for the coating produced with atomized powder feedstock. The comparatively bad wear behaviour of CCA coatings produced with APS in scratch test have to be investigated in more detail. The wear behaviour is probably also influenced by the appearance of pores and oxides, which might be reduced by further optimization of thermal spray parameters.

4 Conclusions

The CCA AlCoCrFeNiTi with equimolar composition has been applied for thermal spray technology in this study. In a first step, feedstock powder was produced by the processes of HEM and inert gas atomization. The process of inert gas atomization proved to be most suitable for the production of homogeneous and spherical powder. Phase analysis revealed two BCC phases in this powder. Both feedstock powders were processed by APS. For the coating produced with atomized powder feedstock, a comparatively more homogeneous microstructure occurs. The investigation of wear behaviour in ball-on-disk and oscillating wear tests revealed superior wear resistance for the coating produced with atomized powder feedstock. In these tests, the wear resistance was also superior to the hard chrome plating. However in scratch tests, the coating produced with atomized powder feedstock showed lower wear resistance than the hard chrome plating. This behaviour might also be influenced by the presence of pores and oxides, which can be reduced by further optimization of thermal spray parameters.

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