Influence of the production route on the phase formation, microstructure and wear behaviour of the high-entropy alloy AlCoCrFeNiTi₀.₅

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Abstract. Different manufacturing approaches have been investigated regarding their suitability to process high-entropy alloys (HEAs). However, comprehensive investigations on the influence of the production route on the microstructure, phase formation and properties have not been conducted yet. For the current study the alloy AlCoCrFeNiTi₀.₅ is considered. Previous investigations have proven the formation of phases with predominantly body centred cubic structure for this alloy. Castings are produced by arc-melting. Feedstock material for coating deposition and powder metallurgical processing is produced by inert gas atomisation. For the processing high-velocity-oxygen-fuel (HVOF) thermal spraying and spark plasma sintering (SPS) are applied. Due to the significantly differing process conditions and temperature-time profiles, differences of microstructure, phase formation and resulting properties can be observed. Wear investigations under various conditions have been conducted. Especially under sliding and reciprocating wear conditions the structural defects formed for the thermally sprayed coating cause a reduction of wear resistance. The formation of structural defects could be avoided by SPS. However, the additional tetragonal phase causes a reduction of the wear resistance. The current study contributes to a better understanding of the interaction between process, microstructure and properties.

1. Introduction

High-entropy alloys represent a new approach of alloy development. They are composed of at least five components mixed in approximately equimolar composition. A promising combination of properties could be proven e.g. high strength and hardness in combination with a pronounced ductility. Furthermore, a high corrosion and wear resistance was observed, making them an interesting candidate for coating applications [1].

One of the first HEAs identified to form a stable single-phase face centred cubic (fcc) structure was the equimolar alloy CoCrFeMnNi. Starting from this composition, the influence of many additional alloying elements has been investigated. One objective was to form a body centred cubic (bcc) structure to increase the hardness and strength. Aluminium showed a strong influence on the phase formation. For sufficiently high contents a bcc structure could be stabilised [2, 3].

A further improvement of mechanical and tribological properties could be achieved by the addition of titanium. Investigations by Zhou et al. revealed an increase of strength and hardness, caused by the high atomic radius of titanium and the resulting severe lattice distortion. However, high contents of
titanium result in the formation of intermetallic phases and embrittlement [4]. The highest wear resistance was determined for the alloy AlCoCrFeNiTi0.5 [5].

The suitability of different production routes has been investigated for HEAs. Early studies focused especially on the production from the liquid state by casting [6]. Also powder metallurgical processes have been applied. Spark plasma sintering (SPS) enables a fast processing and the suppression of grain coarsening [7]. Furthermore, the material usage can be reduced by limiting the application of HEAs to the surface. Thermal spray processes are widely used to produce coatings for corrosion and wear protection applications. Typical structural defects especially pores and oxides can be reduced by applying high kinetic processes e.g. high-velocity-oxygen-fuel (HVOF) thermal spraying [8]. Also HEAs have already been successfully processed by HVOF [9–11].

Despite various investigations on HEAs considering different production routes, the influence of the production route has not been investigated in detail. In the present comparative study the influence on the microstructure, phase formation and tribological properties of the alloy AlCoCrFeNiTi0.5 is investigated. The wear behaviour is examined under sliding, reciprocating and abrasive conditions.

2. Experimental and materials
In the current investigations different production routes have been considered for the alloy AlCoCrFeNiTi0.5. Castings were produced by arc-melting. The manufacturing conditions have been described in detail in a previous study [5]. Feedstock powder was prepared by inert gas atomisation. For further processing a particle size range of -45 +15 µm was used. Prior to the deposition of coatings, substrates (stainless steel EN 1.4404) were prepared by corundum blasting. The coatings were produced with the HVOF system K2 (GTV Verschleisschutz GmbH, Luckenbach, Germany), with the parameters summarised in Table 1.

| **Table 1.** HVOF coating parameters of the AlCoCrFeNiTi0.5 feedstock powder. |
|-----------------------------------------------|
| **O**₂ | kerosene | **Ar** | nozzle | powder feed rate | spraying distance | relative traverse speed | spray path offset |
|-------|----------|-------|--------|-----------------|------------------|-----------------------|-----------------|
| 850 l/min | 22.5 l/h | 2 x 11 l/min | 100/12 | 2 x 40 g/min | 360 mm | 60 m/min | 5 mm |

Furthermore, the feedstock powder was compacted by spark plasma sintering (SPS). The production parameters have been described in a previous study [12].

A detailed characterisation of the microstructure and phase formation has been conducted for all production routes. Cross-sections were prepared by standard metallographic procedures. For the visualisation of material contrast the cross-sections were investigated in the scanning electron microscope (SEM) LEO 1455VP (Zeiss, Jena, Germany), using the backscattered electron detector (BSD). For the investigation of the powder morphology the secondary electron (SE) detector was used. The chemical composition was determined with the integrated energy-dispersive X-ray spectroscopy (EDS) system EDS GENESIS (EDAX, Mahwah, NJ, USA). For the analyses of the formed phases measurements by X-ray diffraction (XRD) have been conducted with a D8 Discover diffractometer (Bruker AXS, Billerica, MA, USA) using Co Kα radiation.

The influence of the microstructure and phase formation on the resulting properties was determined by microhardness measurements in a first step. The Wilson Tukon 1102 device (Buehler, Uzwil, Switzerland) was used to determine the Vickers hardness HV 0.1.

Furthermore, detailed studies to determine the influence on the tribological properties have been conducted. The sliding wear behaviour was investigated in ball-on-disk test, using the Tetra basalt tester (Tetra, Ilmenau, Germany). For the investigation of the wear behaviour under reciprocating conditions a Wazau SVT 40 device (Wazau, Berlin, Germany) has been applied. The abrasive wear behaviour has been investigated in scratch test with a CSM Revetest-RST instrument (CSM Instruments SA, Peseux, Switzerland). All applied wear test parameters are summarised in Table 2.
Table 2. Wear test parameters.

| parameter           | ball-on-disk test | reciprocating wear test | scratch test |
|---------------------|-------------------|-------------------------|--------------|
| force (N)           | 20                | 26                      | progressive  |
| radius (mm)         | 5                 | time (s)                | force (N)    |
| speed (RPM)         | 96                | amplitude (mm)          | speed (mm/min) |
| cycles              | 15,916            | length (mm)             |              |
| counter-body (µm)   | Al₂O₃ (ø 6 mm)    | Al₂O₃ (ø 10 mm)         | tip          |
| tip                 | truncated          |                         | diamond cone |

The wear depth of the ball-on-disk test was determined by tactile measurements with a Hommel-Etamic T8000 device (Jenoptik, Villingen-Schwenningen, Germany). For the evaluation of the reciprocating wear and scratch test the laser scanning microscope Keyence VK-X200 (Keyence, Osaka, Japan) was used.

3. Results and Discussion

3.1. Feedstock characterisation
The surface and cross-sections of the AlCoCrFeNiTi₀.₅ feedstock powder were investigated in SEM, Figure 1.

![Figure 1](image)

Figure 1. AlCoCrFeNiTi₀.₅ feedstock powder, investigated in SEM (SE/BSD): (a) surface and (b) cross-section.

Due to the feedstock production by gas atomisation a spherical powder morphology occurs, enabling a good flowability of the feedstock. In the cross-section a distinct material contrast can be observed, indicating the formation of a heterogeneous microstructure and a deviation of local chemical composition.

3.2. Chemical composition
The mean chemical composition was measured by EDS measurements for all production routes, Table 3.
Table 3. Chemical composition measured by EDS, in at.%. 

| sample                  | Al  | Co  | Cr  | Fe  | Ni  | Ti  |
|-------------------------|-----|-----|-----|-----|-----|-----|
| nominal                 | 18.2| 18.2| 18.2| 18.2| 18.2| 9.1 |
| casting                 | 20.0| 17.8| 17.4| 17.6| 18.2| 9.0 |
| feedstock powder        | 20.1| 17.5| 18.0| 17.9| 17.5| 9.0 |
| HVOF coating            | 19.7| 17.7| 17.6| 18.2| 17.8| 9.1 |
| SPS                     | 21.0| 17.3| 17.7| 17.5| 17.5| 8.9 |

The measured chemical composition is in accordance with the intended values. Only the aluminium contents show a deviation of ≥ 1 at.%. Processing of the feedstock powder by HVOF and SPS causes no distinct change of the chemical composition.

3.3. Microstructure and phase formation
The microstructure of the alloy AlCoCrFeNiTi0.5 was investigated in dependence of the production route. Cross-sections were prepared and investigated in SEM, Figure 2.

Figure 2. Microstructural SEM images (BSD) of AlCoCrFeNiTi0.5: (a) casting; (b) HVOF coating and (c) SPS.

A coarse dendritic structure with a distinct material contrast is formed for the casting produced by arc-melting. The HVOF coating exhibits a lamellar structure, comprising oxide lamellae and pores. Within single spray particles material contrast and a dendritic structure can be observed. In comparison with
the feedstock material no grain coarsening occurs due to the relatively low thermal input. Dense AlCoCrFeNiTi_{0.5} alloys were produced powder metallurgically by SPS. No distinct coarsening of the dendritic structure occurs in comparison with the feedstock material.

The phase formation in dependence of the production route was determined by XRD, Figure 3.

![Figure 3. Diffractograms of AlCoCrFeNiTi_{0.5} feedstock powder; casting; HVOF coating and powder metallurgically produced alloy (SPS).](image)

The diffractogram of the feedstock powder exhibits main diffraction peaks of a chemically ordered bcc phase with B2 structure. Furthermore, a shoulder towards higher diffraction angles occurs at 51.8° and 98.2°, indicating the presence of a second minor phase. These peaks can be assigned to a chemically disordered bcc phase with A2 structure. The casting produced by arc-melting also shows intensity maxima of the bcc phases with B2 and A2 structure. An additional peak occurs at 30.9° indicating the presence of a minor phase with fcc structure. Further peaks of this phase overlap with the bcc phase with B2 structure. The diffractogram of the HVOF coating shows no distinct change in comparison to the feedstock powder. Additional minor diffraction peaks prove the formation of a further chemically ordered bcc phase with B2 structure with a distinctly changed lattice parameter. Powder metallurgical processing causes the formation of an additional tetragonal σ-phase. The formation of this phase in dependence of the manufacturing conditions for the alloy AlCoCrFeNiTi_{0.5} has already been described in previous studies [13].

The effect of the microstructure and phase formation on the resulting properties was investigated by means of microhardness measurements in a first step, Figure 4.
For the casted AlCoCrFeNiTi$_{0.5}$ alloy a hardness of 630 ± 30 HV 0.1 was measured. The coating produced by HVOF exhibits a similar hardness. The deviation is within the range of standard deviation. For the powder metallurgically produced alloy a distinct increase of hardness occurs. A value of 780 ± 50 HV 0.1 was measured. Phase analyses revealed the formation of an additional σ-phase with tetragonal structure. A significant hardening of HEAs by the formation of an additional σ-phase has been described in literature by Tsai et al. [14]. Furthermore, the average hardness can be influenced by the strong variation of grain size (Figure 2).

3.4. Wear behaviour

The wear behaviour was investigated under sliding, reciprocating and abrasive conditions. The results are summarised in Figure 5. A distinct influence of the production route on the wear resistance can be observed. The highest wear resistance under sliding wear conditions in ball-on-disk test was determined for the casting. Solely solid solutions with cubic structure were formed for this production route. Processing of the alloy by thermal spraying causes a higher wear depth and hence lower wear resistance. This behaviour can be explained by the formation of structural defects especially pores and oxides. The phase composition was not significantly altered in comparison to the casting. Despite the formation of a fine-grained microstructure and the absence of structural defects, the alloy produced by SPS exhibits an increased wear depth in comparison to the casting. Phase analyses revealed the formation of an additional σ-phase for this production route. This phase causes an increase in hardness. However, the fracture toughness and ductility are reduced [14, 15]. The impairment of mechanical properties has a negative influence on the wear resistance.

Higher wear depths were determined for the investigations under reciprocating conditions for all production routes. The results reveal a similar tendency. The highest wear resistance was achieved for the casting.

For the investigations under abrasive wear conditions in scratch test a less pronounced dependence on the production route occurs. The highest wear resistance was determined for the casting. Structural defects of the coating cause a slight increase of the wear depth. The additional σ-phase formed for the SPS sample causes no distinct impairment of wear resistance under abrasive conditions.
Figure 5. Results of wear investigations: (a) ball-on-disk test; (b) reciprocating wear test and (c) scratch test.

4. Summary and Conclusions
The influence of the production route on the microstructure, phase formation and wear behaviour was investigated in detail for the alloy AlCoCrFeNiTi0.5. A two phase microstructure comprising two body centred cubic phases was formed for the feedstock powder. In comparison with the arc-melted alloy a minor face centred cubic phase is suppressed. Due to the increased cooling rate, a fine-grained microstructure is formed for the atomised powder. Processing of the powder by thermal spraying causes no major changes of the phase composition. However, typical structural features of thermal spray coatings were identified. Dense material can be produced by spark plasma sintering. No distinct grain coarsening occurs for both processes. However, due to the increased heat input in comparison to the thermal spray process, an additional \(\sigma\)-phase with a tetragonal structure is formed.

The \(\sigma\)-phase and the formation of a fine-grained microstructure cause an increase of microhardness in comparison to the casting. For the thermally sprayed coating no distinct change of hardness in comparison to the casting occurs.

A dependence of wear behaviour on structural features and additionally formed phases was observed, especially under sliding and reciprocating conditions. Despite the coarse-grained microstructure, the highest wear resistance was observed for the casted alloy comprising solely body centred cubic phases. The structural features formed for the coatings cause a reduction of wear resistance. Although these defects were not formed for the powder metallurgically processed alloy, a reduced wear resistance was determined in comparison with the casting. This behaviour is a result of the additional tetragonal \(\sigma\)-phase.
Suitable HEA compositions have to be identified in subsequent studies to avoid the formation of the \(\sigma\)-phase for all production routes. Thus, the equilibrium state has to be considered. For the improvement of coating properties, the content of porosity and oxides has to be further reduced.

**Funding**

This research was funded by the German Research Foundation (Deutsche Forschungsgemeinschaft/DFG), Grant No. La-1274/54-1.

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