



# Exploring the compositional parameter space of high-entropy alloys using a diffusion couple approach

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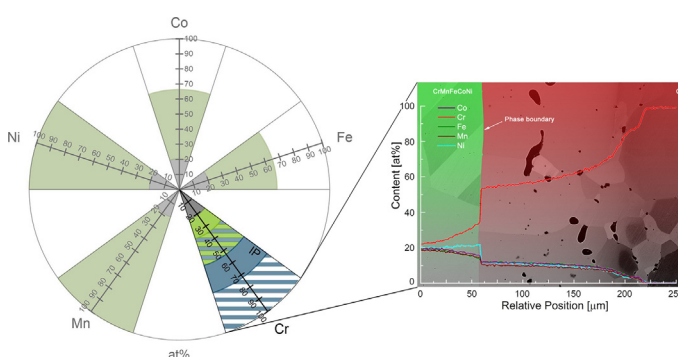
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## HIGHLIGHTS

- Continuous screening of the chemical composition space of high-entropy alloys based on diffusion couples
- Visualization of stability ranges for single phase solid solutions and intermetallic compounds in a comprehensive way
- Derivation of stability ranges for single phase solid solutions and intermetallic compounds
- Model of valence electron concentration for stable cubic solid solutions can be applied over large concentration intervals

## GRAPHICAL ABSTRACT



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## ABSTRACT

In this paper the phase stability and solubility limits of high-entropy alloys are studied, using a diffusion couple approach. Diffusion couples have been fabricated using the established Cantor alloy (CrMnFeCoNi) and a commercial fcc CoNiCrMo alloy (MP35N®) with constituent or foreign elements as diffusion partners. Chemical gradients within the interdiffusion zone as well as the phase stability are quantified using EDX and EBSD. For comparability of the results, new phase stability diagrams are presented. The experimental results show no general correlation between maximum solubility of individual elements and atomic size mismatch, whereas the valence electron concentration model (VEC) seems to be a good approximation for fcc to bcc phase transitions for most of the investigated diffusion couples.

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## 1. Introduction

Over the last decade, the attention to a novel class of alloys called high-entropy alloys (HEA) has increased significantly. By definition, these alloys contain at least five principal elements, each with a concentration of minimum 5 to maximum 35 atomic percent (at.%). [1–3] Furthermore, a single-phase solid solution is often considered as another

mandatory criterion. The high-entropy alloys with five principal elements offer a huge parameter space for numerous alloys with potentially interesting properties. [4] Various alloys have already been developed and characterised from this vast compositional range, yet, it remains widely unexplored. [4,5]. So far, mainly equiatomic systems have been investigated in literature, which was driven by the idea of entropy maximisation [1,6]. One of these alloys is the prototypical equiatomic and nowadays well known CrMnFeCoNi alloy, which was first studied by Cantor et al. [7] and shows a single face-centered cubic (fcc) solid solution. Recent studies [8–11] on the thermal stability of

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the Cantor alloy have revealed the formation of precipitates at temperatures below 800 °C. Thus, even the Cantor alloy does not fulfil the single-phase criterion. However, information on the phase stability and the property range is hardly available in case of changing and non-equiatomic compositions. This understanding is essential for both alloy optimisation and fundamental scientific topics like solid solution strengthening or phase stability including the role of valence electron concentration and atomic size misfit. [12–16]

The diffusion couple technique or the modification to diffusion multiples are promising methods for investigating phase space, phase stability and mechanical properties over a wide range of compositions. [17,18] Franke et al. [17] investigated binary diffusion couples combining EDX with nanoindentation and discussed the results in terms of solid solution strengthening. Additionally, diffusion couples are used to study diffusion or diffusional interactions in high-entropy alloys and to discuss the phenomenon of “sluggish-diffusion”. [19,20] Using diffusion multiples, at least three components are placed in direct diffusional contact to each other. In this way, information about phase stability, mechanical properties and diffusion kinetics can be obtained for higher-order systems much faster than with conventionally produced alloys. The development of high-entropy alloys can be accelerated by using the resulting contour maps of composition, hardness and stability parameters of the quinary region. [21–24]

The objective of this work is to present possibilities and opportunities of the diffusion couple approach for investigation of the phase stability of high-entropy alloys over wide concentration intervals in a continuous manner. For this purpose, we developed a diffusion couple technique to explore in a continuous approach the chemical composition space of two different alloy systems. To investigate the phase stability of high-entropy alloys, we changed the chemical composition continuously starting from the base alloy. This allows to identify composition-dependent structural discontinuities and to screen the property range of the two different alloy systems. Phase stability is studied by a combination of energy dispersive X-ray spectroscopy (EDX) and electron backscatter diffraction (EBSD). The investigated diffusion couples are based on a commercial fcc CoNiCrMo alloy (MP35N®) and the established CrMnFeCoNi Cantor alloy. The CrMnFeCoNi alloy is the most well-known and investigated high-entropy alloy, but due to the higher total number of elements a more complex system. In addition, the four-component CoNiCrMo alloy provides further scenarios encouraging that this approach can be applied to subsets of high-entropy alloys to investigate entire compositional ranges of individual constituent elements and not only an increase compared to the nominal composition.

## 2. Experimental procedure

Diffusion couples of the homogenised  $\text{Co}_{35.8}\text{Ni}_{35.3}\text{Cr}_{22.9}\text{Mo}_{6.0}$  medium-entropy alloy (MEA) and the  $\text{Cr}_{20.7}\text{Mn}_{18.5}\text{Fe}_{20.2}\text{Co}_{20.5}\text{Ni}_{20.1}$  Cantor alloy were prepared with all constituent pure elements as well as Fe as foreign element in case of the CoNiCrMo alloy. The purity levels of the diffusion partner elements Cr, Mn, Fe, Co, Ni and Mo show purity

levels of 99.95%, 99.8%, 99.85%, 99.9%, 99.0% and 99.98%, respectively. The commercial CoNiCrMo alloy was used in a fully annealed condition and the Cantor alloy was synthesized by using an inductive furnace under inert atmosphere followed by a homogenization step as described in [25].

Fig. 1 schematically shows the experimental approach to generate diffusion couples. The contact areas of both the alloy and diffusion partner elements were polished down to  $\frac{1}{4}\ \mu\text{m}$  diamond suspension. For the diffusion bonding step, the samples were mounted in a Mo sample holder and a load was applied by screws. Subsequently, a two-step heat treatment consisting of a diffusion bonding process and a high temperature interdiffusion heat treatment was performed. The diffusion welding process was carried out in a furnace under inert argon atmosphere at different temperatures between 1000 °C and 1250 °C for 1 h. In the next step, the welded specimen was sealed in quartz tubes at 0.3 bar argon atmosphere to perform the final heat treatment under inert conditions. In order to create a sufficiently large interdiffusion zone, a final heat treatment was carried out for 24 h at temperatures that were selected according to the material combination, followed by water quenching. Due to the low melting point of Mn, the CrMnFeCoNi + Mn diffusion couple was diffusion welded and heat treated at 1000 °C, all other diffusion couples were diffusion welded at 1250 °C and heat treated at 1150 °C. For chemical and structural investigations within the interdiffusion zone, cross sections were prepared and polished up to a mechano-chemical treatment with a colloidal silica suspension. The chemical and structural characterization was carried out at a scanning electron microscope (TESCAN Mira3). The concentration profiles within the interdiffusion zone were measured by EDX (energy dispersive x-ray spectroscopy) line scans using 20 kV acceleration voltage, a dwell-time of 200 ms, a step size of 1  $\mu\text{m}$  and 32 to 64 frames. The phase analysis was performed using electron backscatter diffraction (EBSD).

## 3. Microstructural and chemical analysis

By combining the chemical analysis with the results of EBSD measurements, maximum solubility limits of individual elements in the matrix of the base alloys can be observed in detail. During the interdiffusion process, three different cases can be identified for both alloy systems. Fig. 2. gives examples for the single phase case (a.): CrMnFeCoNi + Ni), the formation of an intermetallic phase (b.): CrMnFeCoNi + Cr) and the occurrence of a phase transition from fcc to bcc (c.): CrMnFeCoNi + Fe). Table 1 and 2 provide an overview of the element concentrations at the phase transitions from the base alloys to the respective diffusion partner elements.

### 3.1. Single phase

If nickel is used as a diffusion partner element, the fcc crystal structure of both investigated alloys extends over the entire compositional range (Fig. 3 a.) - b.)). For the CoNiCrMo + Ni diffusion couple, the

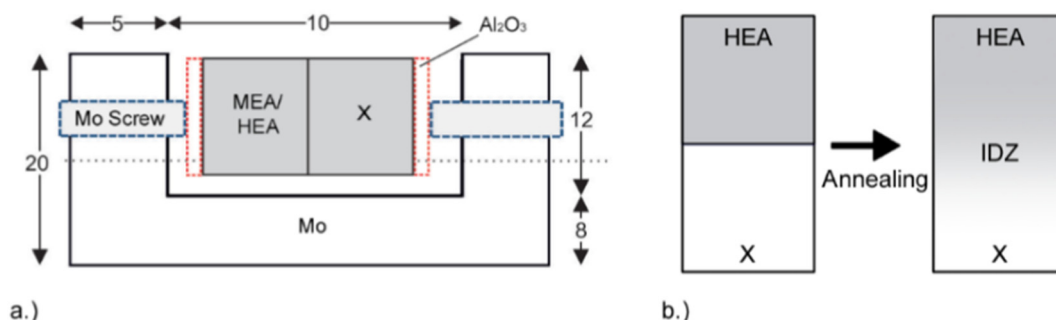


Fig. 1. Schematic diagram of a.) assembly of the diffusion couples (adapted from ur Rehman [26]), b.) formation of the interdiffusion zone (IDZ) during heat treatment.

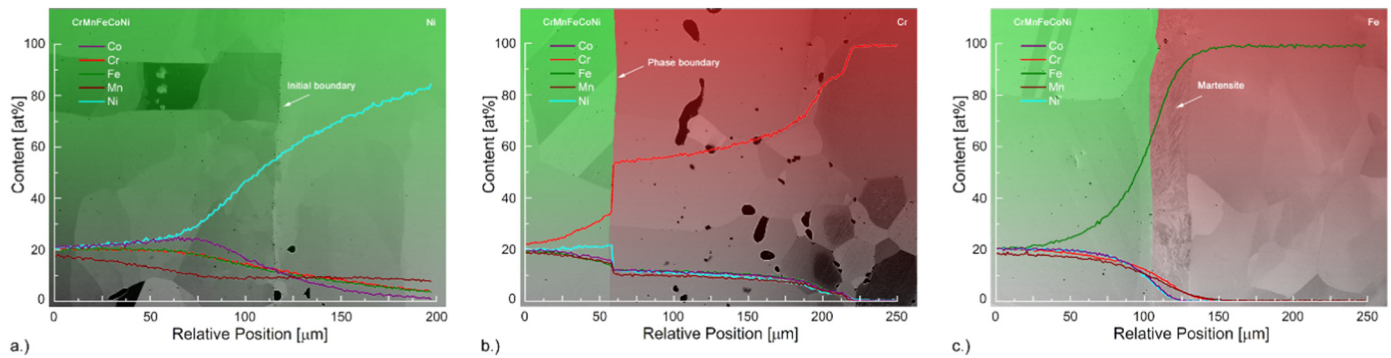


Fig. 2. BSE images with superimposed chemical and phase distribution of CrMnFeCoNi alloy (green) paired with a.) Ni, b.) Cr and c.) Fe.

concentration profile of Ni shows a distinct s-shape within the interdiffusion zone as it is expected for binary diffusion couples from literature (Grube-Jedele solution [27]). An increase in Ni content results in a continuous decrease of all other element concentrations. The changes in element concentrations extend over an interdiffusion zone width of approximately 130 μm. Starting from the equiatomic composition of the CrMnFeCoNi alloy, the Ni concentration shows an s-shaped increase. Up to a distance of approximately 67 μm to the interface, both Ni and Co show an equal concentration level of about 24 at.%. Up to this position the element concentrations of Cr and Fe are almost constant, while the Mn concentration has already dropped to 12.4 at.%. In this region an accumulation of the Co concentration takes place (uphill-diffusion). In the further course, the Mn concentration remains stable over a wide range and Co, Cr and Fe decrease in their concentrations. While the decrease in element concentration is most pronounced for Co, the concentrations of the elements Cr and Fe show a comparable course over the entire width of the diffusion couple.

In case of Mn as diffusion partner element for the CrMnFeCoNi alloy (Fig. 3 c.), the entire concentration profile shows an fcc structure. Accordingly, no phase transition is observed. This seems exceptional as pure Mn only appears above 1095 °C in the closest packed cubic structure [28]. The increase in Mn concentration leads to a decrease in the concentrations of all other constituent elements to the same extent, hence, the concentration profiles of the other constituent elements are similar over the entire concentration interval, which extends over approximately 210 μm.

### 3.2. Phase transition

In contrast to the results using Ni or Mn as diffusion partner elements, an increasing element concentration of Co or Fe causes a phase transition between the two base alloys and the pure element (Fig. 3 d.) – g.).

For CoNiCrMo, the element concentrations can be increased significantly up to approximately 62 at.% Co or 60 at.% Fe until a phase transition to the hcp structure of Co or to the bcc structure of Fe occurs. The

diffusion couple with Co (Fig. 3 d.) exhibits an interdiffusion zone width of approximately 108 μm. Within this compositional interval, Ni shows the strongest decrease in element concentration. An increase in Fe concentration (Fig. 3 e.) results in a collective decrease in all concentrations of the constituent elements. In this case, Ni and Co show a comparable chemical profile and a pronounced decrease in concentrations.

For the CrMnFeCoNi alloy, the chemical gradients also show an s-shaped concentration profile for the diffusion couples based on Co and Fe. The increase in Co content results in a collective decrease of the four other constituent elements. At first Ni exhibits a stable course, but decreases rapidly in the area of the initial interface. The increase in Co content leads to a phase transition of the fcc structure of the alloy to the hcp structure of Co at approximately 66 at.% Co. Due to the element exchange between the alloy and Fe, a phase transition from fcc to bcc can be observed at an Fe concentration of approximately 65 at.%. The increase in Fe results in a decrease of all element concentrations, whereby Co and Ni show a comparable chemical distribution within the interdiffusion zone.

### 3.3. Formation of intermetallic phases

Besides entire single phase and phase transition, a third case can be observed for both alloys, namely the formation of intermetallic phases. By using Cr as a diffusion partner element (Fig. 3 h.) and j.), the fcc phase extends up to approximately 41 at.% Cr for the CoNiCrMo alloy and up to 34 at.% for the CrMnFeCoNi alloy. A further increase results in the formation of intermetallic phases. In case of the CoNiCrMo alloy, the tetragonal sigma (CrFeMo) structure can be assigned to the intermetallic phase. The transition to the intermetallic phase is characterised by abrupt changes in concentrations of all elements. Within the fcc structure of the alloy, the increase in Cr leads to a decrease in Co and Mo content, Ni remains unaffected at a constant level of about 31 at.%. If the diffusion couple is based on the CrMnFeCoNi alloy, the formed intermetallic phase can be indexed as a bcc structure. In the area prior to the phase transition, the elements Co, Fe and Mn are substituted by Cr and Ni (uphill diffusion of Ni). The CoNiCrMo + Mo diffusion couple shows the formation of an intermetallic phase (Fig. 3 i.). Starting

Table 1

Element concentration at phase transition of the diffusion couples based on the CoNiCrMo alloy, entire single phase observed for the diffusion couple with Ni. The diffusion welding process was performed at 1250 °C for 1 h and the final heat treatment was carried out at 1150 °C for 24 h.

Concentration in at.%	Phase transition	Co	Cr	Mo	Ni
Base alloy		35.8	22.9	6.0	35.3
CoNiCrMo + Co	fcc/hcp	61.7	14.4	3.3	20.6
CoNiCrMo + Cr	fcc/sigma	24.8	41.2	3.3	30.7
CoNiCrMo + Fe	fcc/bcc	14.1	9.2	2.1	14.3
CoNiCrMo + Mo	fcc/IP <sup>a</sup>	27.4	19.5	16.0	37.1

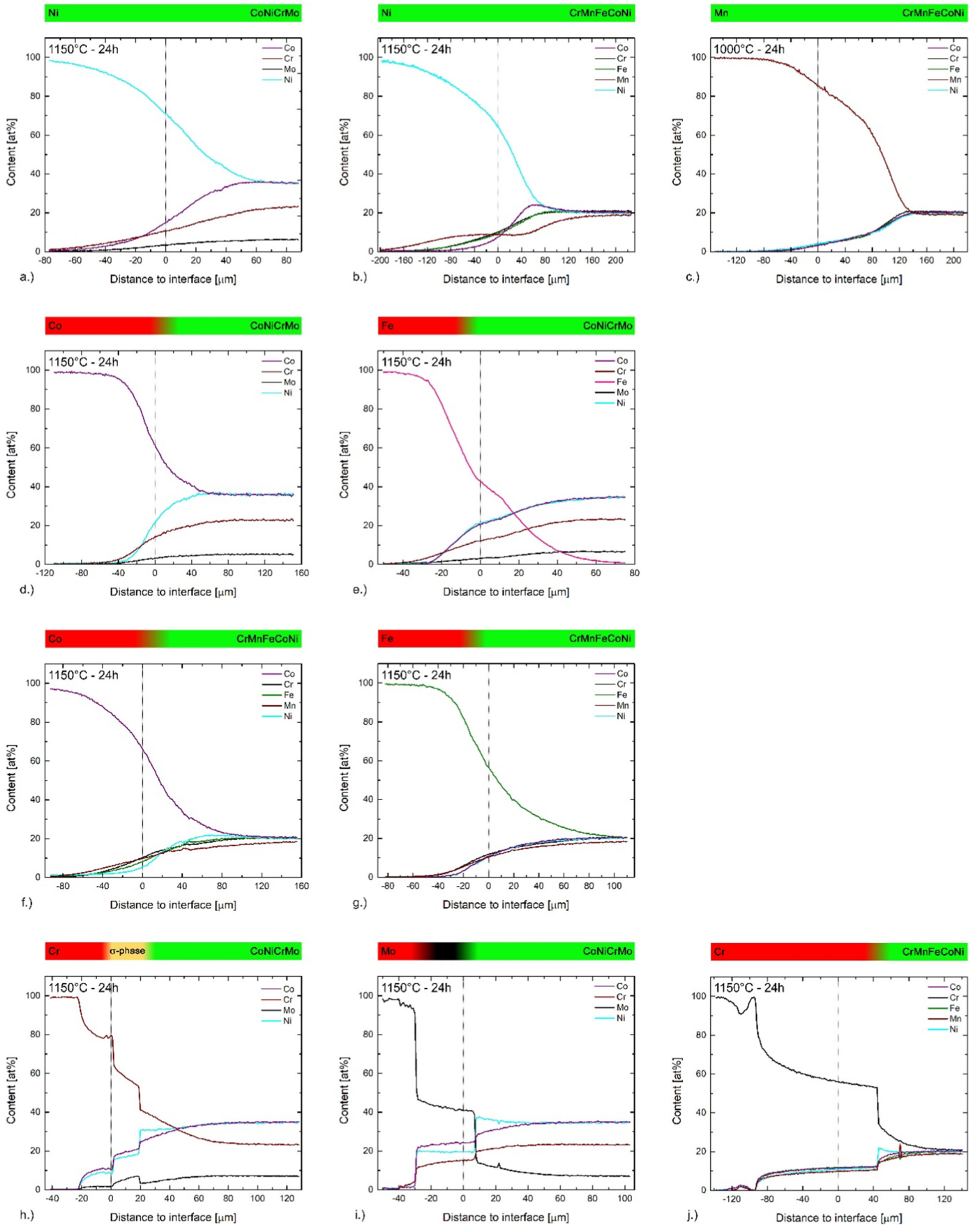
<sup>a</sup> Unknown intermetallic phase, further investigations required.

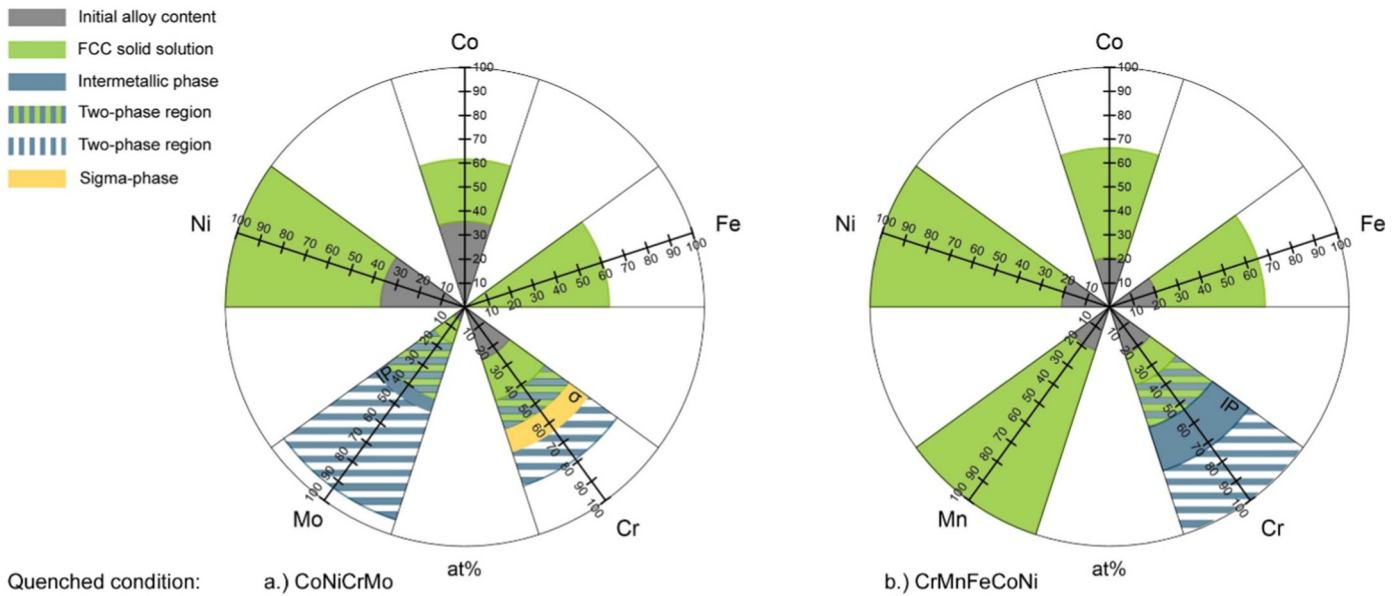
Table 2

Element concentrations at phase transition of the diffusion couples based on the CrMnFeCoNi alloy, entire single phase observed for the diffusion couples with Mn and Ni. The diffusion welding process was performed at 1250 °C for 1 h and the final heat treatment was carried out at 1150 °C for 24 h.

Concentration in at.%	Phase transition	Co	Cr	Fe	Mn	Ni
Base alloy		20.5	20.7	20.2	18.5	20.1
CrMnFeCoNi + Co	fcc/hcp	66.4	10.2	8.1	9.8	5.5
CrMnFeCoNi + Cr	fcc/IP <sup>a</sup>	15.2	34.3	13.8	14.7	22.0
CrMnFeCoNi + Fe	fcc/bcc	8.3	10.0	65.0	8.8	7.9

<sup>a</sup> Unknown intermetallic phase, further investigations required.





**Fig. 4.** Phase stability diagram of a.) CoNiCrMo and b.) CrMnFeCoNi alloy heat treated at 1150 °C (Cr, Mo, Fe, Co, Ni) or 1000 °C (Mn) and quenched to room temperature. The corresponding axis shows the element concentration of the respective diffusion partner element. The diffusion welding process was performed at 1250 °C for 1 h and the final heat treatment was carried out at 1150 °C for 24 h for all samples except CrMnFeCoNi + Mn, which was diffusion welded and heat treated at 1000 °C for 1 h and 24 h, respectively.

from the composition of the base alloy, the Mo content can be increased in the fcc structure up to maximum solubility of 16 at.%. A continuous increase in Mo results in a decrease in Co and Cr concentrations, whereas uphill-diffusion of Ni towards the phase boundary to approximately 37 at.% can be observed. The phase transition is characterised by abrupt changes in all element concentrations. The intermetallic phase shows a constant composition in a width of approximately 36  $\mu\text{m}$ . In contrast to the diffusion couple with Cr, the formed intermetallic phase cannot be indexed as bcc, fcc or sigma phase.

In general, the investigated alloys show for all constituent elements (and Fe as a foreign element in case of CoNiCrMo) large concentration intervals, in which the fcc phase of the alloy remains stable, or metastable as discussed below. The results show a very insensitive response of the alloys to fluctuations in concentrations. In cases where an intermetallic phase is formed within the interdiffusion zone, the maximum amount of alloying element, which can be dissolved in the matrix of the alloy is substantially lower.

To illustrate the formation of secondary phases, BSE (backscattered electron) images with superimposed chemical distribution of the diffusion couples CrMnFeCoNi with Cr and Fe are shown in Fig. 2 b.) and c.) In case of Cr as a diffusion partner element, a grain orientation contrast shift is found at the abrupt change in composition between the fcc structure of the alloy and the intermetallic phase (Fig. 2 b.)). In contrast to this, a secondary phase can also be formed in smooth chemical concentration gradients. The BSE image clearly shows the formation of martensite in the range of higher alloying element concentrations in the bcc solid solution, which exhibits in a width of about 25  $\mu\text{m}$  a different microstructure (Fig. 2 c.)). A change in material contrast is not observable. The position of the phase transition of the fcc structure measured by EBSD corresponds to the phase boundary with the secondary phase, which is visible in the BSE contrast.

There are several scenarios in a single diffusion couple experiments with regard to phase stability, including entire single phase, phase transition between solid solutions or the formation of intermetallic phases (Fig. 2). To visualize the sensitivity to compositional changes with regard to phase stability, the results of multiple diffusion couples can be combined in a spider web like diagram. Fig. 4 shows the dependence of the crystal structure on the chemical composition of the investigated alloys. Each branch represents a single diffusion couple experiment and the corresponding axis displays the composition of the respective diffusion partner element. The grey area indicates the initial content of the respective diffusion partner element in the base alloy. By the diffusive exchange with the pure partner element at annealing temperature, the concentration of this element increases, while all other elements decrease in their concentrations (Fig. 3), which is not shown here. Starting from the equiatomic composition of the Cantor alloy (Fig. 4 b.)), the Fe concentration can be increased up to 65 at.% with alloy remaining in the fcc structure (green area). A higher Fe concentration results in a phase transition from the fcc structure of the alloy to the bcc structure of Fe. In case of a Cr increase (Fig. 4 b.)), the phase of the base alloy remains stable up to 34 at.%. At this point there is a jump in the Cr concentration to 54 at.%, which indicates a two-phase region (green/blue shaded region). The EBSD analysis shows a bcc structure from 55 at.% Cr up to 100 at.%, yet, the shape of the profile with a nearly constant concentration over a certain width indicates an intermetallic phase (blue area). This was also proven by nanoindentation hardness measurements, that are part of an ongoing study, showing a high hardness level of approximately 11 GPa within the flat concentration interval. Considering the limitations of EBSD, further structural investigations are necessary, as the method is not appropriate to determine the crystal structure of an unknown intermetallic phase. The phase transition from the intermetallic phase to pure Cr is also characterised by a jump in concentrations, thus, exhibits

**Fig. 3.** EDX line profiles for the diffusion couples of CoNiCrMo and CrMnFeCoNi with Cr, Mn, Fe, Co, Ni and Mo. Based on the phase analysis, which is represented by a coloured scale on top of each diagram, the diffusion couples are categorised into the three cases single phase (a.) – c.)), phase transition (d.) – g.) and formation of intermetallic phases (h.) – j.)). The initial interface is denoted by a dashed line. The diffusion welding process was performed at 1250 °C for 1 h and the final heat treatment was carried out at 1150 °C for 24 h for all samples except CrMnFeCoNi + Mn (c.)), which was diffusion welded and heat treated at 1000 °C for 1 h and 24 h, respectively.

a two-phase region that extends up to 99 at.% Cr beyond which the bcc structure of Cr becomes stable.

## 4. Discussion

### 4.1. Methodological aspects

Phase formation rules and phase stability are key aspects in the field of research on high-entropy alloys, yet, the terminology can be misleading as phase stability and thermodynamic equilibrium are often not equivalent. Even though numerous high-entropy alloys with a single phase solid solution at ambient temperature have been generated and investigated, it is still unclear whether any of them is actually in thermodynamic equilibrium or all being metastable. One example is the precipitation behaviour of the Cantor alloy, which is still the most common example for a single phase high-entropy alloy, despite being only metastable below 800 °C. [4,8–11] This aspect also affects the apparent phase stability ranges observed along the uniaxial concentration gradients in the diffusion couples, as presented in this work.

In principal, the experimental procedure allows different cooling conditions, such as freezing the condition at the annealing temperature via quenching or slow cooling to approach the thermodynamic equilibrium of the system. Low cooling rates or additional dwell times at lower temperatures would be the obvious choice for studies on thermodynamic equilibria and decomposition tendencies of high-entropy alloys. In this study, the specimen was quenched and phase stability is considered as states that can be kept stable at ambient temperature despite being potentially metastable. This approach would be a preferred choice for investigations of properties in single phase solid solutions over a wide compositional range such as solid solution hardening.

It is also possible to separate between phase transitions that already occurred during interdiffusion annealing and those that occurred upon cooling. During annealing, the system is in thermodynamic equilibrium with respect to local chemistry and there are no changes to local chemistry upon water quenching. Consequently, phase transitions that show discontinuities and accumulations in the concentration profile were already present during annealing and the discontinuities correspond to a two-phase region, where intermediate concentrations do not exist on a local scale (e.g. CoNiCrMo + Mo, CoNiCrMo + Cr and CrMnFeCoNi +

Cr). The accumulation in Ni concentration prior to the phase transition can be explained by a narrow concentration interval within the intermetallic phases. Phase transitions with a smooth concentration profile on the other hand must have formed during cooling. One example for a smooth concentration gradient is the CrMnFeCoNi + Fe diffusion couple. This diffusion couple exhibits an fcc structure over the entire concentration range at an annealing temperature of 1150 °C. Upon water quenching, Fe transforms to bcc structure for Fe concentrations above 65 at.%. This leads to the observation of a phase boundary at room temperature across a smooth diffusion gradient. Such a phase transition violates Gibbs phase rule and cannot exist in thermodynamic equilibrium at annealing temperature, but must have formed during water quenching. Based on this information, the phase stability diagram at annealing temperature is presented in Fig. 5 and discussed below.

While diffusion couples show a huge potential for providing a comprehensive view on phase stability ranges and phase transitions with limited experimental effort, there are also limitations to the method that have to be considered. An increase of the alloying or foreign element that is used in the diffusion couple not only results in a decrease of the other constituent elements but also changes their concentration ratios due to the different diffusivities of the elements involved. These deviations can be negligibly small such as in the CrMnFeCoNi + Mn case, where the diffusion couple resembles a quasi-binary phase diagram within the limitations discussed above (Fig. 3 c.). However, the trajectory through the multi-dimensional phase diagram of high-entropy alloys can also be more complex and far from linear in case of uphill diffusion (e.g. CrMnFeCoNi + Ni) or the occurrence of intermetallic phases during diffusion annealing (Fig. 3 b.).

Thus, the diffusion couple technique facilitates to analyse a wide range of concentrations, but a direct control of the composition is not feasible. The technique therefore is a good approach to screen the property range of medium- and high-entropy alloys over a wide compositional range, but it cannot replace the selective production of individual alloy compositions.

Furthermore, the concentration profiles as well as the phase stability ranges can be used for a comparison with existing results from Calphad simulations. Bracq et al. [29] have calculated the stability ranges in the Cantor alloy using the Calphad method and the TCHEA1 database by varying the concentration of each element in the Cantor system, while

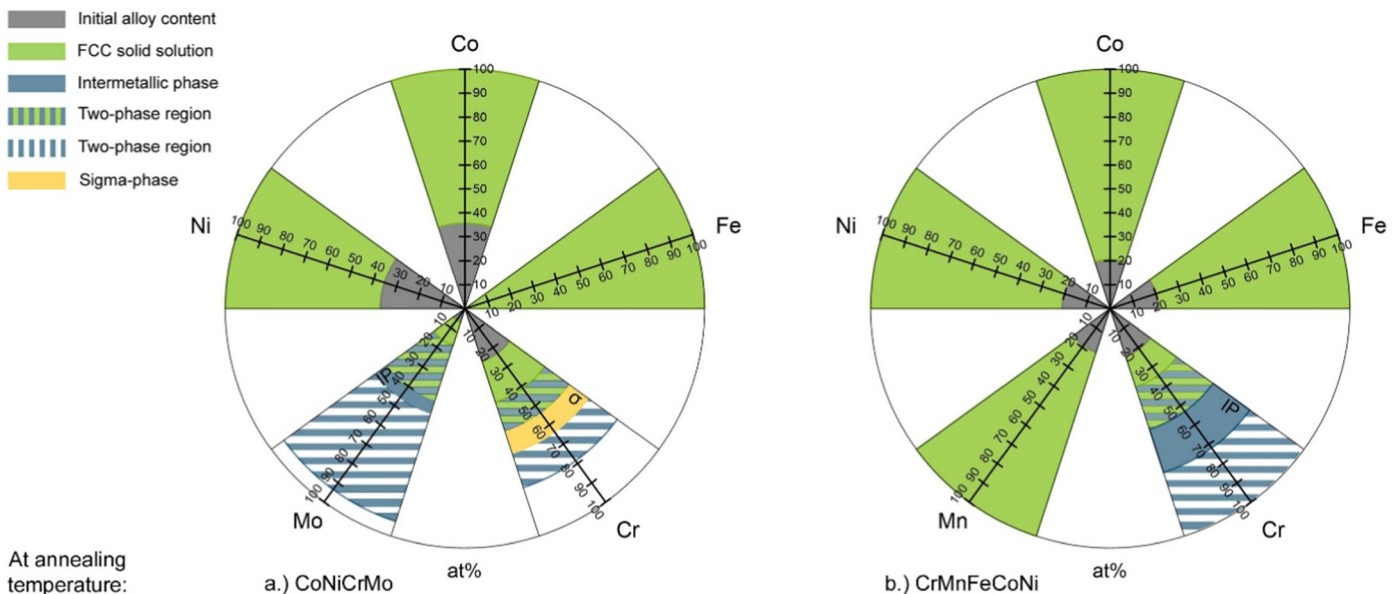


Fig. 5. Phase stability diagram of a.) CoNiCrMo and b.) CrMnFeCoNi alloy at annealing temperature, based on the shape of the concentration profiles. The diffusion couples with Cr, Mo, Fe, Co and Ni were heat treated at 1150 °C, the diffusion couple CrMnFeCoNi + Mn was heat treated at 1000 °C.

keeping all other elements in equimolar proportion. In case of an addition of Co, Fe and Ni the simulations show a complete miscibility (single phase fcc) between the pure element and the CrMnFeCoNi alloy at an annealing temperature of 1150 °C. This is confirmed by the present concentration profiles (Fig. 3), which exhibit no discontinuities for those diffusion couples, thus, indicating an entire single phase range at the annealing temperature (Fig. 5) as has been discussed above. The solubility limit of Cr in the fcc structure of the Cantor alloy at 1150 °C was determined by Calphad to approximately 30 at.%. The present work shows a maximum solubility of about 34 at.%. The small deviation could be attributed to the fact that not all elements change in the same ratio and an uphill diffusion of Ni occurs at the interface. Furthermore, the simulations show a two-phase region (fcc + bcc) in a Cr concentration interval from approximately 30 to 55 at.%. This corresponds well with the concentration interval of the discontinuity in the concentration profile (Fig. 3 j.) from approximately 34 to 53 at.% Cr, to which a two-phase region is assigned (Fig. 5 b.)

According to Bracq et al. [29], Mn destabilizes the fcc solid solution, however, the present results show a single fcc phase over the complete concentration interval. This behaviour cannot be explained at the moment and requires further investigations.

#### 4.2. Application to phase stability

The well-defined concentration gradient within the interdiffusion zone of diffusion couples can be used to investigate fundamental scientific aspects such as the phase stability of high-entropy alloys over a wide concentration interval with limited experimental effort. By superimposing the chemical concentration gradients with phase distribution on a local scale, an insight into the phase stabilising factors can be obtained. One benefit of this method is that not only individual alloy compositions are considered, but also concentration intervals. Two parameters to describe the phase stability of high-entropy alloys are the atomic size mismatch parameter  $\delta$  and the valence electron concentration (VEC). [13,14] The continuous measurement of the chemical concentration facilitates the determination of a composition-dependent atomic size mismatch and valence electron concentration distribution within the interdiffusion zone. In this way, the influence of these parameters on phase stability can be mapped.

#### 4.3. Phase stability criteria: atomic size mismatch

The effect of the atomic size mismatch on the phase formation is not subjected to strict limits, it should be considered as a reference. The atomic size mismatch parameter  $\delta$  can be determined according to Eq. 1 as a function of the chemical composition [13]:

$$\delta = \sqrt{\sum_{i=1}^N c_i (1 - r_i / \bar{r})^2} \quad (1)$$

where N is the total number of elements,  $c_i$  is the concentration in at.% of the  $i$ th element,  $\bar{r} = (\sum_{i=1}^N c_i r_i)$  represents the average atomic radius and  $r_i$  is the atomic radius, which is obtained from literature [30]. The chemical compositions respectively the  $\delta$ -intervals within the intermetallic phases (see Tables 3 and 4) can be used to complement the results of Zhang et al. [13]. The diffusion couples formed on the basis of the

**Table 4**  
Atomic size mismatch of base alloy and intermetallic phase.

Diffusion couple	Atomic size mismatch		
	Base alloy	Phase transition	Intermetallic phase
CoNiCrMo + Cr	2.85	2.47	2.79
CoNiCrMo + Mo	2.85	3.77	5.38
CrMnFeCoNi + Cr	0.92	0.99	0.99

CoNiCrMo alloy are located in a  $\delta$ -range in which both single phase solid solutions and ordered or intermetallic phases occur. Thus, the results of the CoNiCrMo alloy confirm the dependency of the crystal structure on the atomic size mismatch, which is shown in literature. Due to the very similar atomic radii of the constituent elements of the Cantor alloy, fluctuations in element concentrations do not affect the atomic size mismatch parameter.

#### 4.4. Phase stability criteria: valence electron concentration

Another application of the diffusion couples that is related to phase stability is the interpretation of the results with regard to the valence electron concentration (VEC). Since the VEC directly affects the phase stability, Guo et al. [14] presented a statistical analysis (Fig. 6) to describe the phase formation of cubic solid solutions as a function of the valence electron concentration and adapted specific alloy compositions and calculated the valence electron concentrations. Since each composition must be produced individually, they vary in processing and are associated with much experimental effort. According to the observed crystal structures, they defined two threshold values for the formation of fcc and bcc solid solutions.

Based on the chemical gradients at phase transitions, valence electron concentration intervals can be calculated for the different diffusion couples. The CoNiCrMo and the CrMnFeCoNi base alloys show valence electron concentrations of 8.5 and 8, respectively. In case of the CoNiCrMo alloy, an increase in the concentrations of the bcc elements Cr, Mo and Fe results in a decrease of the VEC. The phase of the base alloy (green area) remains stable up to valence electron concentrations of 8.0 (+Cr), 8.3 (+Mo) and 8.2 (+Fe). Thus, the phase transition of the fcc medium-entropy alloy takes place at or before the mentioned threshold value of 8.0. Since the diffusion couples with Cr and Mo show the formation of intermetallic phases, a VEC interval can also be obtained for the compositions within these phases (blue area). No VEC is assigned to the concentration intervals within a discontinuity in the profile. The VEC at phase transitions of the CrMnFeCoNi alloy may provide information on the applicability of the model to five-component alloys. The concentrations within the fcc structure of the alloy show a VEC interval from 8.0 of the base alloy to 7.75 at phase transition when using Cr as diffusion partner. Therefore, the measured phase transition takes place in a VEC interval, in which a transition would be expected according to the model. In the same way, VEC intervals can be assigned to the intermetallic phase or to the phase of the diffusion partner element (grey area).

However, there are also limitations to the applicability of this model. The diffusion couple CrMnFeCoNi + Cr shows a transition from an

**Table 3**

Stability range of the intermetallic phases. The diffusion welding process was performed at 1250 °C for 1 h and the final heat treatment was carried out at 1150 °C for 24 h.

Concentration in at.%	Co	Cr	Fe	Mn	Mo	Ni
CoNiCrMo + Cr	21.0–17.1	53.8–63.9	–	–	7.0–3.2	18.2–15.8
CoNiCrMo + Mo	24.7–21.6	15.6–11.9	–	–	40.4–46.3	19.3–20.2
CrMnFeCoNi + Cr	12.1–7.7	53.6–71.3	12.1–8.2	10.4–6.5	–	11.8–6.26

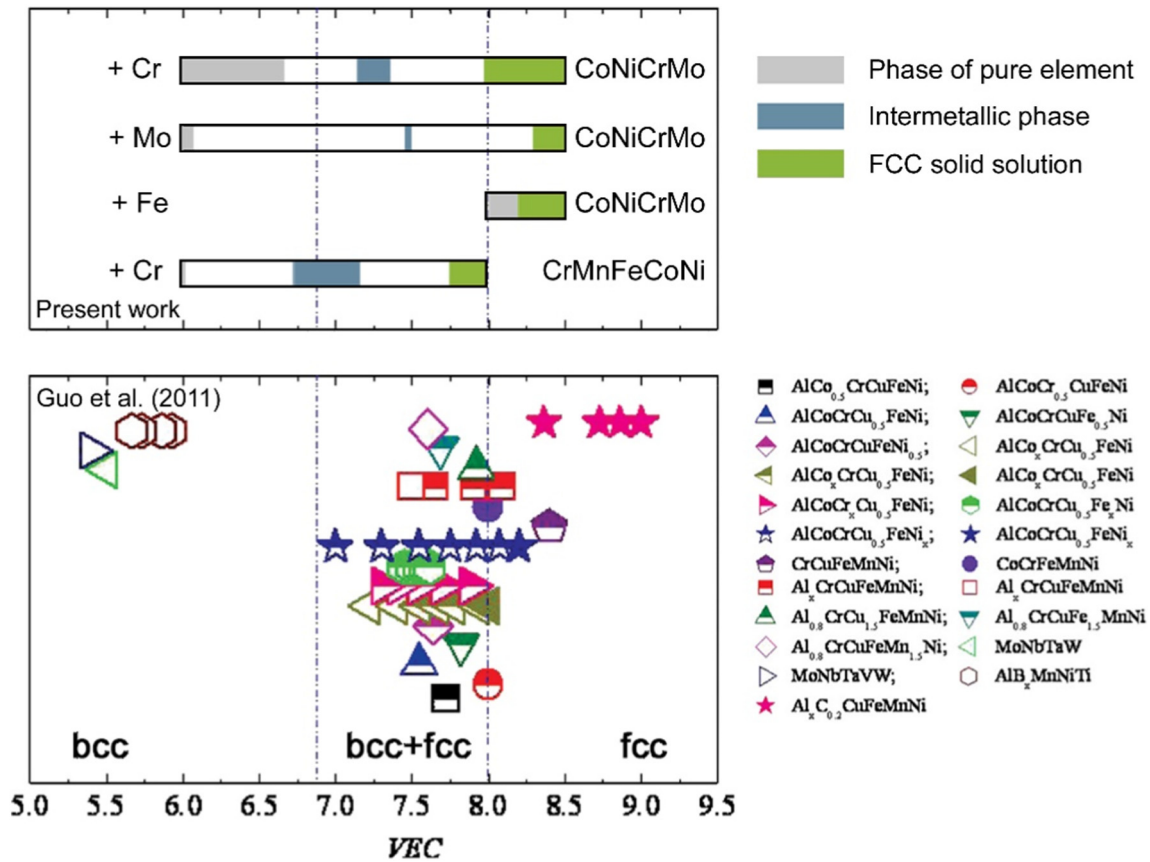


Fig. 6. Model of valence electron concentration for prediction of stable cubic phases. In addition to the statistical results of Guo et al. [14] (lower section of the figure), the measurements of this work are also shown for the CoNiCrMo and CrMnFeCoNi alloy systems (upper section of the figure).

ordered to a disordered bcc structure, which is not considered in the VEC model. The model also fails to predict the phase transition from fcc to bcc that is observed in the CrMnFeCoNi + Fe diffusion couple. Here, the VEC remains constant (8) over the entire interdiffusion zone due to the fact that the change in concentrations of Co and Ni (VEC > 8) is compensated by a change in concentration of Cr and Mn (VEC < 8). Furthermore, the threshold values mentioned in the work of Guo et al. [14] can only be considered as an estimate, given that they depend on the cooling rates [31]. The frequently used fast cooling rates in literature allow a comparability to the present results, where samples were also quenched. Yet, this implies that the stability ranges of the VEC model include metastable ranges, whereas the thermodynamic equilibrium at low temperatures may not be a single phase solid solution, as it has been demonstrated by the decomposition behaviour of the Cantor alloy. [8–10]

#### 4.5. Further applications

Phase stability is a key aspect in research on high-entropy alloys, however several other aspects can be addressed using diffusion couples. One example is solid solution strengthening, which is still not fully understood for high-entropy alloys [4,5,16]. Here, diffusion couples provide the possibility to investigate the mechanical properties as a function of the chemical composition within the interdiffusion zone. The comparison of chemical composition and hardness distribution can reveal information about the solid solution strengthening behavior in chemically complex systems. Another application example could be related to diffusion properties of high-entropy alloys including the validation of modelling approaches for (inter)diffusion, which is beyond the scope of the current work.

## 5. Summary & conclusion

The aim of this work was to investigate the potential and limitations of a diffusion couple approach for high-entropy alloys as well as to apply this approach to address phase stability aspects of such alloys. Diffusion couples of the CoNiCrMo and CrMnFeCoNi alloys were prepared with constituent and foreign pure elements as diffusion partner. The uniaxial concentration gradients and the phase distribution within the interdiffusion zone were measured by a combination of EDX and EBSD.

- 1.) The diffusion couple approach enables investigations on phase stability over a wide compositional range with limited experimental effort. Since the samples were quenched, phase stability measurements consider potentially metastable phases, which can be kept stable at ambient temperatures.
- 2.) Three scenarios with respect to phase stability can be observed, including single phase, phase transition or the formation in intermetallic phases. A phase stability diagram is presented to visualize the solubility limits of individual elements in the investigated fcc high-entropy and medium-entropy alloys.
- 3.) Various approaches for predicting phase stability of high-entropy alloys have been discussed based on the atomic size mismatch or the valence electron concentration (VEC). While the atomic size mismatch describes the formation of intermetallic phases in the CoNiCrMo alloy, the prediction of the structure is insufficient for the CrMnFeCoNi alloy. The present results mostly validate the model of valence electron concentration for predicting stable cubic solid solutions. Hence, the threshold values defined by Guo et al. [14] provide an indication for describing the phase stability with the exception of the fcc to bcc transition with increasing Fe concentrations, which is not covered by the VEC model.



4.) Diffusion couples enable the study of quaternary and quinary intermetallic phases within the chemical composition space of high-entropy alloys. Intermetallic phases, which have already formed during annealing are represented by discontinuities in concentrations. The identification and characterization of these phases is important, as the experimental data on quaternary and quinary intermetallic phases currently still relatively limited.

#### CRedit authorship contribution statement

**Tom Keil:** Investigation, Data curation, Formal analysis, Validation, Visualization, Writing - original draft, Writing - review & editing. **Enrico Bruder:** Conceptualization, Methodology, Validation, Formal analysis, Writing - original draft, Writing - review & editing, Project administration. **Karsten Durst:** Conceptualization, Methodology, Writing - review & editing, Supervision, Project administration, Funding acquisition.

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#### Conflicts of interest

The authors declare no conflict of interest.

#### Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.matdes.2019.107816>.

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