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Combined tracer/interdiffusion measurements in CoCrFeMnNi HEA

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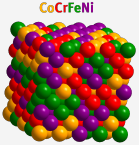
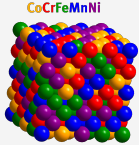
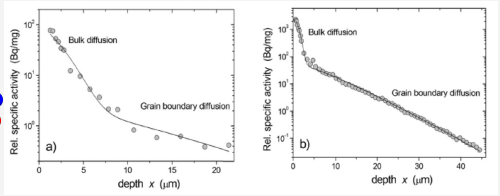
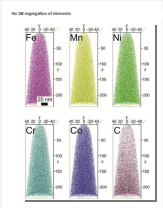
Motivation

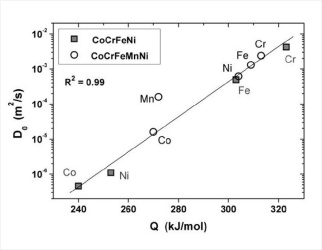








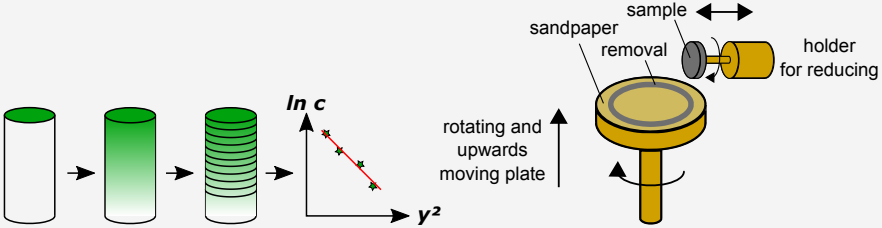
- High-entropy alloys have four or more components in equiatomic proportion
- A “core effect” based on interdiffusion measurements*: “sluggish diffusion”
- Composition dependent atomic mobilities: combination of tracer and chemical diffusion measurements
- Shape of first measured penetration profiles** are not fully understood yet
- **First tracer diffusion experiments in HEA single crystals**



* Yeh et al. Acta Mater (2013)
** Vaidya, Divinski et al. JALCOM (2016)
Vaidya, Divinski et al. Sci Rep 7 (2017)
Vaidya, Divinski et al. Acta Mater 146 (2018)

Radiotracer technique

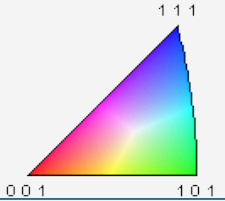
- Single crystal samples pre-annealed at 1100 °C for 3 days
- Self-diffusion: annealed at 1100 °C for different times
- Cu-diffusion: annealed at 700 °C for 12 hours, at 800 °C for 2 hours and at 900 °C for 20 minutes

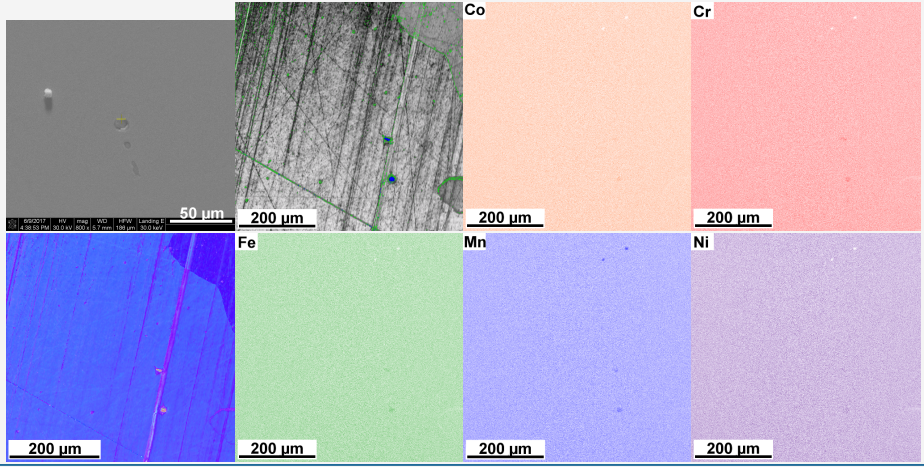


- Sectioning procedure performed by mechanical grinding (self-diffusion) and ion-beam sputtering (Cu-diffusion)
- $D_v = -\frac{1}{4t}\left(\frac{\partial \ln \tilde{c}}{\partial y^2}\right)^{-1}$

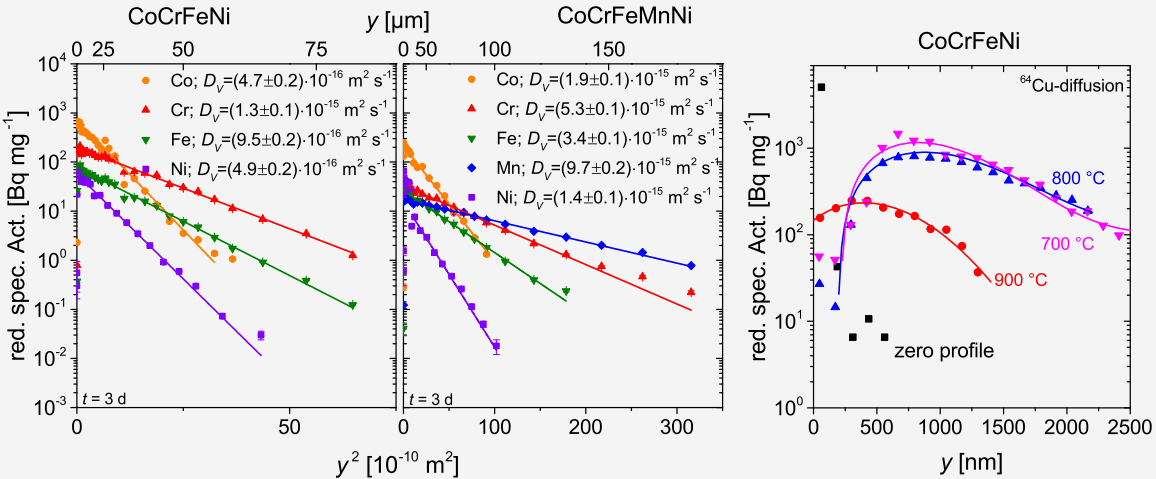
CoCrFeMnNi ‹111› microstructure (1100 °C, 3 d)

Element	*c* [at. %]
Co	19.9
Cr	19.4
Fe	19.6
Mn	20.2
Ni	20.9





Penetration profiles



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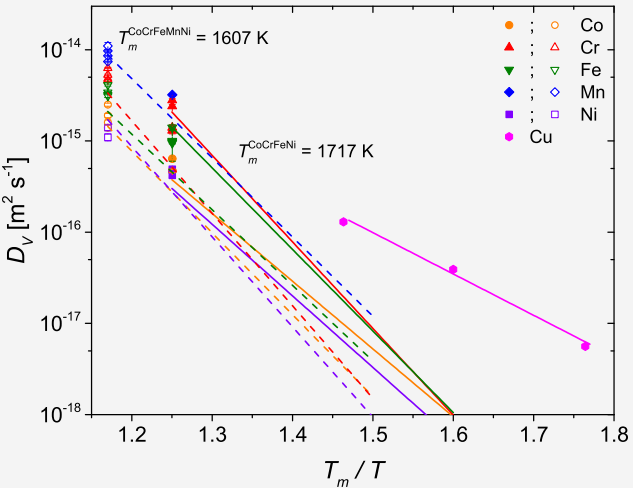
Arrhenius plot

CoCrFeNi

Element	D_0 [$m^2\ s^{-1}$]	$-\Delta H$ kJ mol^{-1}
Co	$7.15 \cdot 10^{-7}$	244
Cr	$1.52 \cdot 10^{-3}$	312
Cu	$6.23 \cdot 10^{-10}$	149
Fe	$2.15 \cdot 10^{-4}$	294
Ni	$1.95 \cdot 10^{-6}$	258

CoCrFeMnNi

Element	D_0 [$m^2\ s^{-1}$]	$-\Delta H$ kJ mol^{-1}
Co	$4.52 \cdot 10^{-5}$	276
Cr	$2.46 \cdot 10^{-3}$	312
Fe	$1.05 \cdot 10^{-5}$	255
Mn	$1.25 \cdot 10^{-4}$	267
Ni	$6.24 \cdot 10^{-4}$	304



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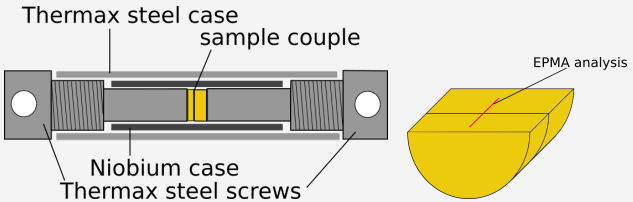
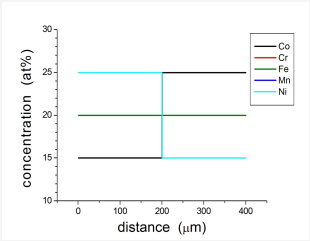
Experimental procedure

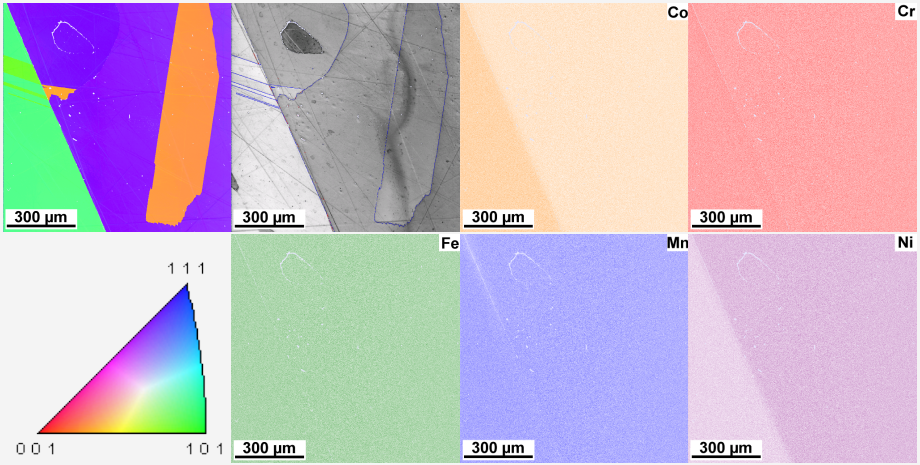
- $Co_{15}CrFeMnNi_{25}$-$Co_{25}CrFeMnNi_{15}$ high entropy alloy pseudo-binary couple arc melted and homogenized at 1200 °C for 2 days
- Diffusion annealed at 1100 °C for 2 days



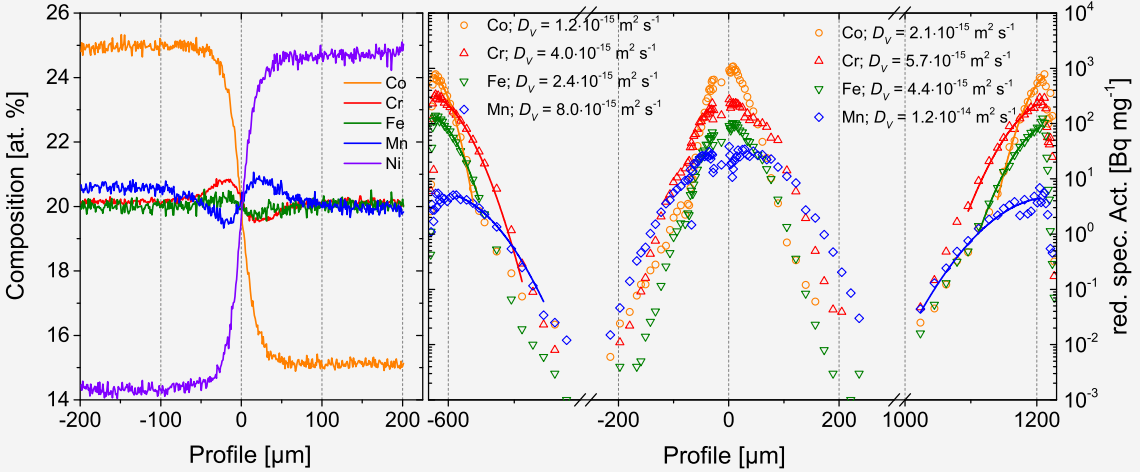


- Chemical diffusion: Interface analyzed by EPMA
- Radiotracer diffusion: Tracer were applied on both surfaces of both samples; sectioning of the samples by mechanical grinding (s.a.)

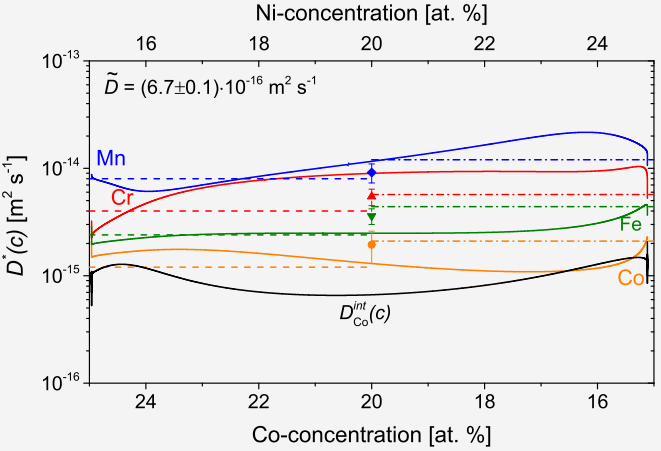
Microstructure analysis



EPMA & tracer analysis



Composition dependent atomic mobilities



Darken-Manning equation*:

$$D_{\text{D-M}} = (N_{\text{Co}} D^*_{\text{Co}} + N_{\text{Ni}} D^*_{\text{Ni}}) \cdot (\Phi S)_{\text{Co-Ni}}$$

$$\Rightarrow (\Phi S)_{\text{Co-Ni}} = 1.1 \pm 0.2$$

Thin layer isotope sandwich configuration**:

$$D^*(c) = -\frac{\frac{(y+a)}{2t} - G(y)\frac{1}{c(y)}}{\frac{\partial \ln c^*(y)}{\partial y} - \frac{\partial \ln c(y)}{\partial y}}$$

* Darken Transactions AIME 147 (1948)
* Manning Acta Metall. 15 (1967)
** Belova, Murch et al. Phil. Mag. Let. (2015)

Summary

- Bulk diffusion results in single crystals are in good agreement with bulk diffusion results in polycrystals
- Diffusion is time-independent and isotropic
- Mn is the fastest element, Ni the slowest element in both systems
- Tracer diffusion is not retarded (”sluggish”) with addition of a further alloying element in equiatomic proportion
- Cu is fastest element at 900 °C and below (low activation enthalpy)

Summary

- Bulk diffusion results in single crystals are in good agreement with bulk diffusion results in polycrystals
- Diffusion is time-independent and isotropic
- Mn is the fastest element, Ni the slowest element in both systems
- Tracer diffusion is not retarded (”sluggish”) with addition of a further alloying element in equiatomic proportion
- Cu is fastest element at 900 °C and below (low activation enthalpy)
- No loss of Mn, but Mn evaporates at interface with large gap
- Up-hill diffusion in HEAs pseudo-binary approach
- Almost ideal solid solution alloy after Darken-Manning
- Faster tracer diffusion in Ni-rich part
- Asymmetrical tracer diffusion profiles at interface
- S-shape of concentration dependent Co-tracer diffusion coefficient at 15 at. % $< y_{Co} <$ 25 at. %

Outlook

- Arrhenius-dependence of self-diffusion in CoCrFeNi and CoCrFeMnNi single crystals down to 600 °C
- Cu-diffusion in CoCrFeMnNi single crystals
- Mn-diffusion in CoCrFeNi single crystals
- Grain-boundary diffusion in CoCrFeNi and CoCrFeMnNi bicrystals
- TEM analysis of the dislocation network

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- Combined interdiffusion and tracer-diffusion experiments for $Co_{23}CrFeMnNi_{17}$-$Co_{17}CrFeMnNi_{23}$ at 1100 °C for 2 days
- Combined interdiffusion and tracer-diffusion experiments for $Co_{25}Cr_{15}MnNi$-$Co_{15}Cr_{25}MnNi$ (including Arrhenius-dependence)
- Simulations of the composition dependent atomic mobilities (see the following talk by Katrin Abrahams!)

Acknowledgements

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