EUROPEAN ORGANIZATION FOR NUCLEAR RESEARCH

Proposal to the ISOLDE and Neutron Time-of-Flight Committee

Radiotracer diffusion in refractory high-entropy alloys

October 4, 2016

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CERN-INTC-2016-044 / INTC-P-477
04/10/2016

Abstract: High entropy alloys (HEAs) are multicomponent alloys with a large number of constituent elements in equiatomic or nearly equiatomic composition. Sluggish atomic diffusion is believed to represent one of the core effects in HEAs which is presumably responsible for their unique properties. The current proposal is focused on tracer diffusion in the five-component AlScTiZrHf high-entropy alloy which can undergo ordering under thermal treatment. The ISOLDE facility provides ^{46}Sc/^{48}Sc and ^{173}Hf radioisotopes which otherwise are not available. Combined with the tracer diffusion measurements of the isotopes ^{44}Ti and ^{95}Zr, which will be performed in Münster, an extensive dataset will be gained on atomic mobilities in this alloy. The direct diffusion measurements shall be combined with density-functional-theory calculations of point defects and jump barriers which will be done in the research group of Dr. B. Grabowski (MPIE Düsseldorf). We intend to prove an anticipated tendency to a successive slow down of the tracer diffusion rates with an increased number of components in equiatomic alloys. Simultaneously the importance of both, the entropy term, especially the correlation factor, as well as the energy barriers shall be analyzed in detail.

Requested shifts: 11 shifts over 3 years

1. State of the art and preliminary work

State of the art. High entropy alloys (HEAs) are multicomponent alloys developed based on a design concept of multi-principal elements. They are available in equiatomic or nearly equiatomic proportions [1, 2]. HEAs have been explored for high temperature applications [2] and understanding their creep properties and the involved diffusion kinetics is of critical importance. Furthermore, reliable diffusion data are required as a key input for rigorous phase prediction using, e.g. the CALPHAD approach [3]. HEAs represent (by definition) single phase materials but the thermal stability to decomposition or ordering is often questioned [4]. There are numerous experimental indications that second phases or local order are appearing after thermal treatment at moderate temperatures [5].

The appearance of second phase particles or element ordering with formation of specific sub-lattices can provide promising ways to improve the mechanical properties of HEAs. For example, ordered phases are rather frequently found in bcc structures [6] and a modulated structure of a solid solution composed of disordered bcc A2 and ordered B2 and L12 has been observed in AlCoCrCuFeNi [2]. Diffusion measurements provide a sensitive and often a unique method to investigate the kinetic stability of these alloys against phase decomposition and/or ordering.

Astonishingly, only very few experimental studies have been published so far on the direct investigation of diffusivities in high entropy alloys and the majority of them were focused on *interdiffusion measurements*. Tsai et al. [7] have determined the interdiffusion coefficients for a composition $CoCrFeMn_{0.5}Ni$ which corresponded to the Kirkendall plane in that experiment. Their analysis (and the main conclusion about so-called *sluggish* diffusion in HEAs) was rather limited in view of the vague assumptions on the value of the thermodynamic factor (just unity) and because of overlooking completely the off-diagonal terms in the Onsager matrix. Kulkarni and Chauhan [8] determined the diffusion matrix in CoCrFeNi at 1000°C from an interdiffusion experiment and have argued that the role of diffusional interactions is very important in HEAs. Dabrowa et al. [9] have studied interdiffusion in non-equiatomic AlCoCrFeNi alloys and they highlighted the importance of crystallographic parameters in determining the diffusion behavior in HEAs, rather than simply attributing it to varying chemical environments.

Very recently the Münster group published a first report on *tracer* diffusion measurements in CoCrFeNi and CoCrFeMnNi HEAs [10]. It was shown that at any given absolute temperature the diffusion rate in the five-component alloy is even faster than that in the four-component alloy. Thus, the addition of components to equiatomic alloys does not inevitably retard the atomic diffusion rate.

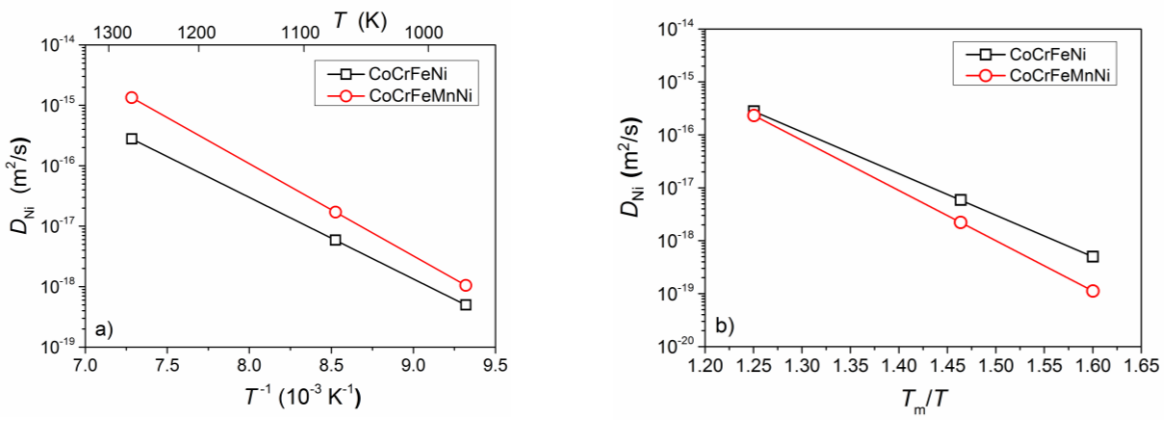
We conclude that astonishingly the present knowledge on HEAs is contradictory to some extent. In fact, the term 'sluggish diffusion' seems to be a fixed and non-separable term for the HEA concept. On the other hand, the only available tracer diffusion data published for the CoCrFeMnNi HEA question strongly this hypothesis. Unfortunately, the tracer diffusion data are completely missing for others HEAs. Are the findings of Ref. [10] generally applicable? Does a hypothetical diffusion retardation depend on the particular type of lattice (BCC, HCP)? The answers to these questions which are crucial to developing the fundamental understanding of HEAs can only be found by dedicated experimental studies.

Preliminary work. Diffusion investigations, mainly with radioactive isotopes, have a long-standing tradition at the Institute of Materials Physics of Münster University. There exists a fully-equipped laboratory for radioisotope storage and handling, including mechanical grinder

and ion-beam sputtering devices for serial sectioning and both β- and γ-radiation counting facilities of remarkably low backgrounds.

The applicant has a profound experience in grain boundary diffusion measurements in pure metals and alloys, e.g., he contributed to the majority of diffusion experiments on low-temperature (the so-called C kinetic regime) solute diffusion available in the literature, see e.g. [11-14]. Furthermore, what is most relevant for the proposed project, the previous research was focused on diffusion in intermetallic compounds, especially in ordered Ni-Al, Ti-Al, Fe-Al intermetallics, see e.g. [15, 16]. A combination of experimental measurements and atomistic simulations was often used for establishing the basic diffusion mechanisms in ordered compounds [16]. These results were partially summarized in textbooks [17, 18].

Tracer diffusion in HEAs. As it was already mentioned, recently we measured Ni tracer diffusion in CoCrFeNi and CoCrFeMnNi HEAs [10] which crystallize in the FCC structure upon quenching. The alloys were prepared by casting and then homogenized by annealing at 1200°C for 50 hours. Tracer diffusion of ^{63}Ni was measured in the two HEAs and the Arrhenius plot is presented in Fig. 1 as a function of the inverse, $1/T$, and inverse homologous, T_m/T, temperatures (here T_m is the melting point of the corresponding compound).



a) b)

Figure 1: Diffusion of ^{63}Ni in CoCrFeNi and CoCrFeNiMn HEAs as plotted against inverse temperature $1/T$ (a) and the inverse homologous temperature T_m/T (b). Here T_m is the melting point of the alloys.

Our study on the FeCoCrMnNi high-entropy alloys suggests that the so far in the literature anticipated 'high-entropy' effect on diffusion retardation is *not* supported by the direct tracer measurements! If the tracer diffusion rate is considered at a constant temperature, the Ni diffusion rate is even enhanced by addition of Mn to FeCoCrNi alloy, Fig. 1.

The diffusion rates of different elements in the FeCoCrMnNi HEA are substantially different [19], see Fig. 2. Mn is the fastest element, while Co and Ni are the slowest elements at higher or lower temperatures, respectively.

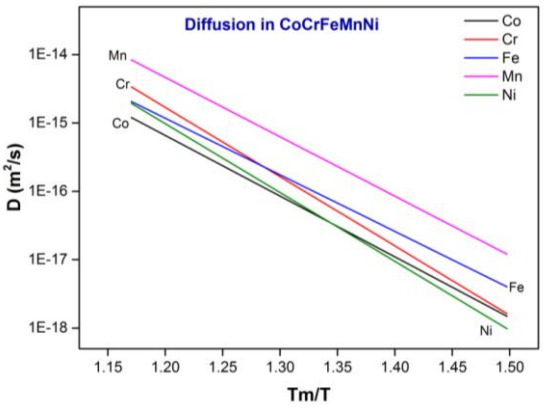


Figure 2: Diffusion rates of all constituent elements in equiatomic FeCoCrMnNi as investigated by the radiotracer method using the ^{59}Fe, ^{57}Co, ^{51}Cr, ^{54}Mn, and ^{63}Ni radioisotopes plotted against the homologous temperature T_m/T.

These studies confirm the significant knowledge of the PI in the field of tracer diffusion studies. An extension of the measurements to other systems, especially to BCC or HCP alloys is required. A key and decisive issue is a simultaneous determination of diffusion properties of all principal elements of the high-entropy alloy in question. Since not all isotopes are freely available on the market, the usage of special facilities such as ISOLDE is required for some particular isotopes, like Sc.

2. Research objectives and planned experiments

Research objectives. The current proposal is focused on a detailed characterization of atomic diffusion in refractory HEAs. The compositions of $Al_{15}H_{25}Sc_{10}Ti_{25}Zr_{25}$ and $Al_5H_{25}Sc_{20}Ti_{25}Zr_{25}$ (in at.%) will be prepared by our colleague, Dr. L. Rogal (Institute of Metallurgy and Materials Science of the Polish Academy of Sciences, Krakow, Poland). An ingot of the $Al_{15}H_{25}Sc_{10}Ti_{25}Zr_{25}$ alloy of 10 mm in diameter and 3 mm in height is already available which is enough for the planned experimental research. Further samples will be prepared from pure elements of 99.99 wt.% purity in an arc melting furnace with a water-cooled copper plate under a protective Ar atmosphere. A phase stability will be investigated in AlScTiHfZr alloy alloyed with Cu. In this case diffusion of Cu (the Cu^{67} isotope) is proposed to investigate.

The samples will be fully characterized using available facilities at the Institute of Materials Physics, University of Münster and applying SEM+EBSD, TEM including HR-TEM, DSC, X-Ray, low-temperature heat capacity measurements.

Self-diffusion in refractory HEAs. Tracer diffusion of ^{44}Ti (available) and ^{95}Zr (shall be purchased) are planned to be measured in the radiotracer laboratory in Münster using existing facilities. At the ISOLDE facility, it is planned to measure diffusion of Sc (the ^{46}Sc/^{48}Sc isotopes) and Hf (the ^{173}Hf isotope). In that respect, we will strongly benefit from the experience of our colleagues, research group of Prof. N. Stolwijk (Institute of Materials Physics, University of Münster) which successfully performed ^{43}K diffusion measurements in single-crystal feldspar in July 2016 by using beam-time provided by a cooperation within the INTC-P-261 project (Spokesperson M. Deicher, Saarbrücken). These results are submitted for publication [20] and they demonstrate the feasibility of dedicated radiotracer diffusion experiments with the procedures and equipment available at ISOLDE.

A typical tracer diffusion experiment consists of the following steps (after detailed microstructure characterization and chemical analysis performed in Münster):

a) mechanical polishing of one face to a mirror-like quality and pre-diffusion annealing to remove all preparation-induced defects (shall be done in Münster);

b) ion-beam implantation of a given amount (typically 10^{11} - 10^{12} ions) of the radioactive isotope onto the prepared samples (at ISOLDE), acceleration voltage preferably 50 kV or higher;

c) diffusion-annealing in vacuum or under purified Ar at a temperature *T* for a time *t*;

d) parallel sectioning using an ion-beam sputtering device;

e) measurements of the specific radiotracer activity in each section (i.e. the relative specific radioactivity per section mass), which is proportional to the concentration of the diffused species. A NaI γ-spectrometer is available to measure the intensities of γ-decays;

f) determination of the tracer diffusion coefficients by comparing the concentration-depth profile data obtained from the tracer experiment, with the appropriate solution of Fick's second law.

We are planning to measure the diffusion rates of Hf and Sc atoms at a temperature interval of 800 K to 1600 K which fits the facilities available at ISOLDE developed within the INTC-P-261 project (Spokesperson M. Deicher, Saarbrücken). The diffusion measurements will be performed in two HCP alloys, $Al_{15}H_{25}Sc_{10}Ti_{25}Zr_{25}$ and $Al_5H_{25}Sc_{20}Ti_{25}Zr_{25}$, which reveal presumably different stability towards phase decomposition or ordering.

The steps b) to e) of the experiments (the list above) shall be performed *in-situ* by using an available off-line diffusion chamber (ODC) to be operated in off-line modus. This high-vacuum chamber has been constructed at the University of Saarbrücken and installed at ISOLDE in 2009, first as an on-line device. Later on, during 2016, the ODC set-up was reinstalled for off-line use in the Solid State Physics Lab (Building 508, Room 001) by cooperative efforts of the research group of Prof. N. Stolwijk (Münster) and Prof. M. Deicher (Saarbrücken) groups. The ODC set-up makes it feasible to use the radiotracers with half-lives of even several hours directly at the ISOLDE facility.

^{46}Sc/^{48}Sc diffusion in HEAs. The ^{48}Sc isotope with a half-life of 43.7 h (100% γ-radiation with 1.037 MeV) can be produced from the Ta targets with a fluency of 7.7×10^6 ions/μC. This requires an implantation time of 60 min for collecting about 10^{11} ions per sample. The relative long half-life of the isotope allows an extension of the temperature interval of diffusion measurements to lower temperatures (longer diffusion times). This isotope is preferential since it uses the same target as the second requested isotope, ^{173}Hf (see below), which will allow an optimum usage of ISOLDE beam line.

The ^{46}Sc isotope can be produced from the Ti target with a better fluency as the ^{48}Sc isotope, 7.7×10^7 ions/μC, which implies smaller collecting times of 30 min per sample. This isotope has a suitably long half-time of 83.8 d and a perfect γ-yield (100%, 0.889 MeV) which make it suitable for *off-site* measurements in Münster. In the latter case we can deposit further the ^{44}Ti and ^{95}Zr tracers in our lab in Münster and perform simultaneous measurements of Ti, Sc, and Zr diffusion at exactly the same temperatures. These experiments are suitable for double checking the results.

To characterize the temperature dependence of Sc diffusion in HEAs, we typically need 5 to 6 measured depth profiles arising from annealing at different temperatures. At a selected temperature the effect of annealing on diffusion shall be evaluated. We request 6 shifts over 3 years.

^{173}Hf diffusion in HEAs. The ^{173}Hf isotope with a half-life of 23.6 h (83% γ-radiation with 0.124 MeV) can be produced from Ta targets with a fluency of 2.0×10^{8} ions/μC, which requires a gross implantation time of 30 min for collecting 10^{11} ions per sample. Similarly to the case of Sc, six samples are necessary to determine the temperature dependence of the diffusion coefficients per high-entropy alloy. Hereto, we request 3 shifts over 3 years.

^{67}Cu diffusion in Cu-alloyed AlScTiHfZr. The ^{67}Cu isotope with a half-life of 2.6 d (49% γ-radiation with 0.185 MeV) can be produced from UC_x targets with a fluency of 3.5×10^{8} ions/μC (and from ZrO_2 with 2×10^{7} ions/μC). This requires a gross implantation time of 30 min for collecting 10^{11} to 10^{12} ions per sample. Similarly to the case of Cu-free HEAs, six samples are necessary to determine the temperature dependence of the diffusion coefficients per high-entropy alloy. Hereto, we request 2 shifts over 3 years.

Combined investigations. These measurements will be accompanied by the radiotracer measurements of Ti and Zr diffusion in the same alloys which will be done in Münster, since appropriate isotopes are available. All tracer diffusion measurements will be combined with theoretical studies of jump barriers for self-diffusion. An agreement with Dr. B. Grabowski (MPIE Düsseldorf, Germany) has already been achieved. B. Grabowski is an expert in the field of finite temperature density-functional-theory calculations of defect properties [21] and he will provide a theoretical background for a rigorous interpretation of the diffusion mechanisms.

Summary of requested shifts: 11 shifts

We are ready to share beamlines for ions if this would be required. And we are not limited to the usage of the mentioned isotopes of Sc, Hf or Cu. The main requirement is an acceptable half-life for us (at least 10 hours) and a possibility to use gamma-spectroscopy to detect ions (good yields for gamma-rays).

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Appendix

DESCRIPTION OF THE PROPOSED EXPERIMENT

The experimental setup comprises: *(name the fixed-ISOLDE installations, as well as flexible elements of the experiment)*

Part of the Choose an item.	Availability	Design and manufacturing
SSP-GLM chamber	☒ Existing	☒ To be used without any modification
On-line diffusion chamber	☒ Existing	☒ To be used without any modification, used off-line ☐ To be modified
	☐ New	☐ Standard equipment supplied by a manufacturer ☐ CERN/collaboration responsible for the design and/or manufacturing
Existing equipment (furnaces, glove boxes) in the solid state labs in building 508	☒ Existing	☒ To be used without any modification ☐ To be modified
	☐ New	☐ Standard equipment supplied by a manufacturer ☐ CERN/collaboration responsible for the design and/or manufacturing

HAZARDS GENERATED BY THE EXPERIMENT

(if using fixed installation) Hazards named in the document relevant for the fixed [COLLAPS, CRIS, ISOLTRAP, MINIBALL + only CD, MINIBALL + T-REX, NICOLE, SSP-GLM chamber, SSP-GHM chamber, or WITCH] installation.

Additional hazards:

Hazards			
	SSP-GLM	*On-line diffusion chamber*	*[Part 3 of the experiment/equipment]*
Thermodynamic and fluidic			
Pressure			
Vacuum	10^{-6} mbar during collections	10^{-7} mbar during measurements	
Temperature	Room temperature	< 1500 K	
Heat transfer			
Thermal properties of materials			
Cryogenic fluid			
Electrical and electromagnetic			
Electricity			
Static electricity			
Magnetic field			
Batteries			
Capacitors			
Ionizing radiation			
Target material	AlScTiHfZr		
Beam particle type (e, p, ions, etc)	Ions		

Beam intensity	$< 10^8$ s^{-1}		
Beam energy	50 – 60 keV		
Cooling liquids			
Gases			
Calibration sources:			
• Open source			
• Sealed source		^{22}Na, ^{60}Co sources for detector calibraion	
• Isotope			
• Activity			
Use of activated material:			
• Description	☒ Measurement in ODC or shipping to Münster		
• Dose rate on contact and in 10 cm distance	< 1 mSv/h		
• Isotope	^{46}Sc, ^{48}Sc, ^{173}Hf		
• Activity	All < 15 MBq		
Non-ionizing radiation			
Laser			
UV light			
Microwaves (300MHz-30 GHz)			
Radiofrequency (1-300MHz)			
Chemical			
Toxic			
Harmful	[Acetone (ICSC: 0087), ethanol (ICSC: 0044)], Less than few centilitres per chemical, used for cleaning samples in ventilated fume hood in building 508		
CMR (carcinogens, mutagens and substances toxic to reproduction)			
Corrosive	[HCL], Less than few centilitres per chemical, used for sample preparation in ventilated fume hood in building 508		
Irritant			
Flammable			
Oxidizing			
Explosiveness			
Asphyxiant			
Dangerous for the environment			
Mechanical			
Physical impact or mechanical energy (moving parts)			
Mechanical properties (Sharp, rough, slippery)			
Vibration			
Vehicles and Means of Transport			
Noise			
Frequency			
Intensity			

Physical			
Confined spaces			
High workplaces			
Access to high workplaces			
Obstructions in passageways			
Manual handling			
Poor ergonomics			

0.1 Hazard identification

3.2 Average electrical power requirements (excluding fixed ISOLDE-installation mentioned above): *(make a rough estimate of the total power consumption of the additional equipment used in the experiment)*