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Summary Report of the High Entropy Alloys for Nuclear Applications Workshop

19-21 October 2021,
remotely hosted by CIEMAT

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The mission of the NEA is:

– to assist its member countries in maintaining and further developing, through international co-operation, the scientific, technological and legal bases required for a safe, environmentally sound and economical use of nuclear energy for peaceful purposes;

– to provide authoritative assessments and to forge common understandings on key issues as input to government decisions on nuclear energy policy and to broader OECD analyses in areas such as energy and the sustainable development of low-carbon economies.

Specific areas of competence of the NEA include the safety and regulation of nuclear activities, radioactive waste management and decommissioning, radiological protection, nuclear science, economic and technical analyses of the nuclear fuel cycle, nuclear law and liability, and public information. The NEA Data Bank provides nuclear data and computer program services for participating countries.

Foreword

The Expert Group on Innovative Structural Materials (EGISM) was created in 2008 under the auspices of the Nuclear Science Committee's (NSC) Working Party on Scientific Issues of the Fuel Cycle (WPFC). Its objective is to conduct joint and comparative studies to support the development, selection and characterisation of innovative structural materials that can be implemented in advanced nuclear systems operating under extreme conditions, such as high temperatures, high dose rates, corrosive chemical environments and long-service lifetimes.

In this context, innovative structural materials may comprise, but are not limited to, advanced materials in terms of chemical composition and microstructure developed to have unique properties; materials or material structures created through new manufacturing methods; and advanced materials in terms of design and architecture, including coated systems, such as functionally graded materials. High-entropy alloys (HEAs), which are attracting significant attention in materials science and engineering, in some ways meet all three definitions. Indeed, these materials, which are designed with unique chemical compositions and microstructures to enhance their properties, are mostly designed and produced using new manufacturing methods and/or as coatings or graded systems.

Among the objectives of the EGISM is to provide a state-of-the-art assessment of specific areas that are considered a priority in research, with a view to identifying and developing potential synergies. Therefore, a workshop was organised on high-entropy alloys for nuclear applications as an extension of the EGISM work on the technological assessment of HEAs for use in nuclear systems. This summary report outlines the presentations given during the workshop and the various exchanges held during the sessions, as well as the outcomes of the panel discussion on the opportunities and limitations for HEAs in nuclear systems.

Acknowledgements

The Nuclear Energy Agency (NEA) expresses its sincere gratitude to the members of the Expert Group on Innovative Structural Materials (EGISM) for their help with the organisation of the workshop. Special thanks go to Marta Serrano and Lorenzo Malerba (CIEMAT, Spain) for hosting the event. The NEA also acknowledges Fanny Balbaud, Chair of EGISM, and Céline Cabet, Co-Chair of EGISM for their efforts in preparing this summary report. The Chair and Co-Chair would like to thank Davide Costa (NEA) for his strong support in the organisation of this workshop.

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List of abbreviations

AFA	Alumina-forming austenitic (alloys)
BCC	Body-centred cubic
CCA	Complex concentrated alloy or compositionally complex alloy
CEA	Le Commissariat à l'énergie atomique et aux énergies alternatives (Alternative Energies and Atomic Energy Commission, France)
CENIM	Centro National de Investigaciones Metalurgicas (National Centre for Metallurgical Research, Spain)
CIEMAT	Centro de Investigaciones Energéticas Medioambientales y Tecnológicas (Centre for Environmental and Technological Energy Research, Spain)
CNRS	Centre national de la recherche scientifique (National Centre for Scientific Research, France)
CSA	Concentrated solid solution alloy
EGISM	Expert Group on Innovative Structural Materials (NEA)
FCC	Face-centred cubic
HEA	High-entropy alloy
HVOF	High velocity oxygen fuel spray
ICMCB	Institut de Chimie de la Matière Condensée de Bordeaux (Institute of Condensed Matter Chemistry of Bordeaux, France)
ICMPE	Institut de Chimie et des Matériaux Paris-Est (East Paris Institute of Chemistry and Materials, France)
INL	Idaho National Laboratory (United States)
KIT	Karlsruhe Institute of Technology (Germany)
LMD	Laser metal deposition
MD	Molecular dynamics
MPEA	Multi-principal entropy alloy
NEA	Nuclear Energy Agency
NSC	Nuclear Science Committee (NEA)
ODS	Oxide dispersed strengthened
OECD	Organisation for Economic Co-operation and Development
ORNL	Oak Ridge National Laboratory (United States)
PSI	Paul Scherrer Institute (Switzerland)
RBS	Rutherford backscattering spectrometry
RHEA	Refractory high-entropy alloy
SFE	Stacking fault energy
SFT	Stacking fault tetrahedron
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis
TRL	Technology readiness level

TWI	The Welding Institute Ltd (United Kingdom)
WPFC	Working Party on Scientific Issues of the Fuel Cycle (NEA)
XRD	X-ray diffraction
YS	Yield strength

Executive summary

In October 2021, the Nuclear Energy Agency (NEA) held a workshop on the development, potential uses, opportunities and limitations of high-entropy alloys (HEAs) for nuclear applications. The workshop was hosted by the Centre for Environmental and Technological Energy Research (CIEMAT) in Spain and held online due to the COVID-19 pandemic. In total, 84 participants from 4 continents took part in the workshop.

With the development of advanced nuclear systems, such as Generation IV reactors, the identification of materials that fully comply with the expected requirements for the high performance of these systems is still a work in progress. The purpose of this workshop was to share information on the latest developments and innovations in the field of high-entropy materials to help identify opportunities in the field of advanced nuclear systems. The workshop only included invited plenary lectures by materials scientists with expertise in deploying HEAs for industries and/or expertise in the nuclear sector. This report summarises the presentations and discussions held during the workshop.

As one of the outcomes of this workshop, it can be noted that HEAs will be used in future nuclear applications. Researching HEAs will make it possible to find materials that meet new, high-level requirements. The deployment of HEAs will require the development of reliable manufacturing processes to ensure their advanced properties. Given their probable high costs, HEAs are expected to be mostly used as coatings on conventional alloys and additive manufacturing is an exciting opportunity. The qualification of HEAs for nuclear applications is as challenging as with any new alloy, in particular to obtain properties following irradiation, even more so for fusion-relevant conditions. The use of ion irradiation rather than neutron irradiation is more challenging for HEAs than conventional alloys and will require developing new modelling tools. To accelerate the qualification and deployment of HEAs, it is advised to explore compositional space around the well-understood systems and strengthen dialogue between the HEA and conventional alloy communities.

Workshop agenda

Day 1	**19 October 2021 – General session**	
12:00	Workshop opening	Marta Serrano (CIEMAT, Spain)
12:05	Workshop introduction	Fanny Balbaud (CEA, France), EGISM Chair
12:20	Introduction to HEAs: opportunities and limitations	Daniel Miracle (Materials and Manufacturing Directorate of the US Air Force Research Laboratory, United States)
	Overview on R&D initiatives, session Chair: Lorenzo Malerba (CIEMAT, Spain)	
13:00	US perspective: Tunable chemical disorder in concentrated alloys: Defect properties and radiation performance	Yanwen Zhang (ORNL, United States)
13:30	EU perspective: INNUMAT – perspective and prospective structural materials for fission and fusion	Jarir Aktaa (KIT, Germany)
14:00	*Coffee break*	
14:10	China perspective: One of the materials for future: High-entropy alloys	Yong Zhang (University of Science and Technology Beijing, China)
14:40	End of Day 1	
Day 2	**Technical session**	
	Numerical design, CALPHAD computation, session Chair: Fanny Balbaud (CEA, France), EGISM Chair	
12:00	Numerical design and computational approaches to develop high entropy alloys	Isaac Toda Caraballo (CENIM, Spain)
12:25	Computational thermodynamic and machine learning assisted design of high entropy alloys	Stéphane Gorsse (ICMCB, CNRS, France)
	Fabrication/manufacturing, session Chair: Yong Dai (PSI, Switzerland)	
12:50	Manufacturing of complex concentrated alloys (CCAs): Microstructure, performance and challenges	Francesco Fanicchia (TWI, United Kingdom)
13:15	Design, fabrication and characterisation of Co-free FCC HEAs	Anna Fraczkiewicz (Mines Saint Etienne, France)
13:40	*Coffee break*	

	Phase stability, microstructural characterisation, mechanical testing, session Chair: Yong Dai (PSI, Switzerland)	
13:50	The microstructures and mechanical properties of HEAs	Edward J. Pickering (Manchester University, United Kingdom)
14:15	Mechanical properties and underlying deformation mechanisms of complex concentrated alloys: A review	Jean-Philippe Couzinié (ICMPE, CNRS, France)
14:40	End of Day 2	
Day 3	**Technical session**	
	Compatibility with corrosive environment, session Chair: Céline Cabet (CEA, France), EGISM Co-Chair	
12:00	Corrosion resistance of alumina forming HEA/CCA in steam and liquid Pb alloys	Alfons Weisenburger (KIT, Germany)
12:25	The passivation and corrosion protection mechanisms of MPEAs in aqueous solutions	John R. Scully (University of Virginia, United States)
	Irradiation resistance, session Chair: Jian Gan (INL, United States)	
12:50	Mechanisms of radiation damage build up in high-entropy alloys	Flyura Djurabekova (University of Helsinki, Finland)
13:15	Effect of stacking fault energy on irradiation damage in Co-free high entropy alloys	Naoyuki Hashimoto (Hokkaido University, Japan)
13:40	Theoretical modeling of irradiation damage in high entropy alloys	Shijun Zhao (City University of Hong Kong)
14:05	*Coffee break*	
14:15	*Conclusion: Panel discussion: HEAs for nuclear applications, opportunities and limitations* *Moderator: James Marrow (Oxford University, United Kingdom)* *Confirmed panellists:* *Francesco Fanicchia (TWI Ltd, United Kingdom)* *Edward J. Pickering (Manchester University, United Kingdom)* *Yanwen Zhang (ORNL, United States)*	
15:00	Conclusive remarks	Fanny Balbaud (CEA, France), EGSIM Chair
15:15	End of the workshop	

General sessions

The research and development of HEAs has opened up a new field in materials science. These alloys can be designed as bulk materials or as coatings; can be metallic, ceramic, single-phase or multi-phase; and can be considered for applications as novel structural or functional materials.

At the same time, the development of advanced nuclear systems, such as Generation IV reactors, small modular reactors, transmutation systems and fusion devices, requires high-performance structural materials that must be selected or designed and developed to address the specific challenges of their foreseen operational environments. In several cases, materials that fully comply with the expected requirements for the high performance of these systems have not been identified yet.

The purpose of this workshop was to share information on the latest developments and innovations in the field of high-entropy materials to help identify opportunities in the field of advanced nuclear systems. The workshop only included invited plenary lectures by materials scientists with expertise on deploying HEAs for industries and/or expertise in the nuclear sector.

During the workshop, the following topics were discussed:

- National initiatives to accelerate the development of HEAs for nuclear applications;
- Numerical design of HEAs and modelling;
- Manufacturing of HEAs (bulk materials and coatings);
- Material properties, in-service ageing and microstructure characterisation studies;
- HEAs for nuclear applications, opportunities and limitations.

Although alternative terms have been proposed, such as medium-entropy alloys, multicomponent alloys, compositionally complex alloys, complex concentrated alloys or multi-principal-element alloys, which are close or fully equivalent to HEAs, the EGISM had decided to use the general name “high entropy alloys” because it is now well known by materials scientists and engineers, nuclear system designers, stakeholders and decision makers. The EGISM was informed that no unequivocal definition exists for HEAs and this was further discussed during the workshop.

The workshop featured 15 full-length overview and technical presentations and a panel discussion featuring three panellists. The presentations were organised thematically in sessions chaired by EGISM members. In total, 84 participants from 4 continents took part in the workshop.

Introduction

Welcome addresses were delivered by Marta Serrano, host of the workshop and a EGISM member (CIEMAT, Spain), and Fanny Balbaud, Chair of the EGISM from the Commissariat à l'énergie atomique et aux énergies alternatives (CEA, France). Dr Daniel Miracle (Air Force Research Laboratory, United States) then gave an introductory speech.

Dr Miracle is a senior scientist in the Materials and Manufacturing Directorate of the Air Force Research Laboratory in the United States. His research covered nickel-based superalloys and intermetallic compounds, metal matrix composites, advanced aluminium alloys and boron-modified titanium alloys. His current research focuses on metallic glasses and HEAs. In his speech, he discussed two key concepts about high-entropy alloys: (1) that the stability of solid solutions can be manipulated by adjusting configurational entropy (via the number and concentrations of alloying elements); and (2) that a vast number of new, unexplored materials await discovery. He outlined the initial four core effects on which the concept of a HEA relies:

- from edge to centre of phase diagrams (dilute to concentrated): what does “concentrated” mean?
- from base element to multi-principal element (complex): no obvious, dominant base element;
- from locally disrupted to jumbled atomic structures;
- from dozens to hundreds of billions of compositions.

The speech discussed the new behaviours observed in these materials that lead to new opportunities, such as:

- new dislocation responses;
- improved balance of mechanical properties;
- new environmental properties (e.g. refractory alloys with improved oxidation resistance);
- promising initial results in catalysis;
- more complete control of alloy density.

Approaches for designing and developing HEAs for specific applications were also addressed:

- defining an application;
- selecting the elements and adjusting element selection criteria;
- selecting a microstructural paradigm and using phase diagrams (CALPHAD method);
- screening hundreds of compositions by combining high throughput experiments, machine learning, multi-objective optimisation and expertise.

Finally, Dr Miracle presented a vision of autonomous materials R&D (AMRAD) dedicated to bulk and inorganic materials.

Overview of R&D initiatives

The general session, which covered the national and international R&D initiatives on HEAs, was chaired by Lorenzo Malerba (CIEMAT, Spain). International perspectives from three current programmes were presented.

Yanwen Zhang from Oak Ridge National Laboratory (ORNL, United States) described the US perspective in a talk entitled "Tuneable chemical disorder in concentrated alloys: Defect properties and radiation performance", co-authored with Yuri N. Osetskiy (ORNL, United States) and William J. Weber (ORNL, United States).

Alloys consisting of multiple elemental species, which were referred to as concentrated solid solution alloys (CSAs) in this talk, exhibit intrinsic chemical disorder and therefore also site-to-site lattice distortion, distorted electronic structure, magnetic frustration, aperiodic energy landscapes, etc. As such, they promise to enable the tuning of radiation-induced defect properties (modified migration barriers, reduced diffusion, high recombination probability). The presentation gave an overview of several simulation results, compared with experiments whenever possible, revealing that:

- "electronic disorder", and thus resistivity, can be increased with the inclusion of specific elements or combinations of elements;
- the complexity of mixing elements with a high atomic volume mismatch creates larger distortions and the existence of rough energy landscapes may generate local traps for defects, reducing diffusion and anisotropic diffusion channels;
- the combination of electronic and atomic effects (electron-phonon coupling and energy landscape) may reduce defect production in displacement cascades;
- site-to-site distortion may stabilise specific crystal structures;
- increasing the chemical complexity creates a regime of linear damage accumulation;
- nanostructured alloys, which may also be CSAs, offer another path to reducing radiation damage;
- doped CSAs, i.e. with complex composition and small additions of specific elements, exhibit specific properties, such as lower swelling, via formation of coherent nano-sized particles whose interfaces act as a recombination centre for defects;
- similar effects can be obtained via the oxide-dispersion strengthening (ODS) of CSAs, or via nanostructuring (small grains), although grains grow under irradiation.

In the United States, the selected research pathways to establish radiation resistant metallic alloys are to develop advanced materials in terms of chemical composition and microstructure. This means combining chemical and microstructural complexity.

Jarir Aktaa from the Karlsruhe Institute of Technology (KIT, Germany) gave a presentation on the EU INNUMAT's proposed project on new structural materials development for fission and fusion.

The INNUMAT proposal concerns innovative structural materials for fission and fusion and was submitted in the latest Euratom call, for the part dedicated to advanced structural materials for nuclear applications. The call aims to fund projects that will develop the high-temperature, corrosion and radiation resistance of structural materials, in connection with the operating conditions expected in next generation nuclear systems, such as lead-cooled fast reactors and molten salt fast reactors. The call also asks for applications to fusion reactors.

The analysis of the remaining gaps concerning nuclear materials for advanced systems highlighted, among others, the susceptibility of ferritic/martensitic steels to liquid metal embrittlement and of austenitic steels to liquid metal corrosion, both of which require protection from circulating fluid effects. Addressing these issues requires a holistic approach, which led the work-package breakdown of the project to be organised in terms of materials design, qualification for compatibility, thermal stability and radiation tolerance, and the development of bespoke methodologies for this.

HEAs have been included in the portfolio of materials addressed in INNUMAT. HEAs without Co and containing Al to develop alumina protective layers are envisioned. Other materials included are alumina forming austenitic (AFA) steels, coated 15-15 Ti steels, austenitic steels with FeCrAl weld overlay (all these mainly for fission applications), and alumina coated Eurofer and ODS steels (for fusion applications).

The project is structured in a way that for each material a research track is defined that makes use of the skills and techniques featured by each work package. In the case of HEAs, this gives: (1) developing Co-free HEAs based on Face-Centred Cubic (FCC) CrFeMnNi; (2) exploring new Body-Centred-Cubic (BCC)-HEAs with improved ductility keeping good high-temperature strength; (3) increasing technology readiness level (TRL); (4) developing computational tools to design HEAs using advanced modelling and machine learning techniques. The path goes through alloys design and fabrication, characterisation and iteration towards better properties.

Pr. Yong Zhang (University of Science and technology of Beijing, China) presented the Chinese perspective in a talk entitled "One of the materials for future: High-entropy alloy".

Historically, it is possible to recognise a pattern in materials development towards increasingly higher entropy, culminating with HEAs. HEAs started as single-phase equimolar systems and are now moving towards non-equimolar, more complex compositions and phases. Among the crucial feature of these materials is the possibility of playing with a "cocktail of properties", thus opening the way to innumerable potential applications.

The presentation provided interesting examples, such as (1) a ZrTiNb alloy with simultaneously very high strength (yield > 1 000 MPa) and good ductility; (2) NbMoTaW with much better compressive ductility than W; (3) VCrFe(TaW)0.2 with simultaneously above average yield strength and compressive ductility.

The origin of HEAs' radiation resistance was discussed and attributed to at least three factors:

- contrary to long-range one-dimensional (1-D) motion in most conventional metals, the 3-D migration path of interstitials in HEAs increases recombination with vacancies;
- atomic level stresses facilitate amorphisation and local melting with more efficient recrystallisation;
- a shorter electron mean free path (higher thermal resistivity) prolongs the thermal spike and further favours recovery.

Other properties and applications were discussed, such as: (1) soft magnetic materials; (2) corrosion resistant materials; (3) solar absorber coatings (high thermal stability, corrosion resistance, high absorption efficiency); (4) flexible films.

Overall, these alloys offer the possibility of unprecedented combinations of functional and mechanical performances.

Technical session

Numerical design and CALPHAD computation

This session, chaired by Fanny Balbaud (CEA, France), included two presentations addressing various aspects of computationally assisted design of HEAs.

Isaac Toda Caraballo from the National Centre for Metallurgical Research (CENIM, Spain) gave a presentation on numerical design and computational approaches that develop high-entropy alloys. In this presentation, he reviewed different computational design strategies, which offer new compositions in HEAs:

- new solid solution formation rules for advancing HEAs discovery;
- development of new and more extensive databases for CALPHAD calculations;
- use of atomistic simulations, although the progress made in new interatomic potentials have been limited in comparison to the above-mentioned computational techniques.

Alloys of interest in nuclear applications were analysed, such as FCC CrFeMnNi alloys, and BCC HEAs: MoNbTaVW (microstructural stability, high-temperature mechanical properties), AlCrMoNbZr (corrosion resistance, high hardness), TiVNbTa (low brittle-ductile transition temperature), HfNbTaTi (good damage tolerance and negligible irradiation hardening).

Stéphane Gorsse from the Centre national de la recherche scientifique (CNRS, France) gave an overview of the computational thermodynamics and their value to gain a better understanding of the relationship among atomic composition, process and microstructure in order to predict the phases that are formed, their volume fractions and their transformation temperatures. This knowledge will enhance the development of advanced alloys with carefully designed microstructures and enhanced properties.

More recently, machine learning has also emerged as a technique to predict complex properties by learning from the data.

The following items were addressed and discussed in more detail:

- CALPHAD method (minimisation of the Gibbs free energy): from known binary and ternary subcomponent systems, the CALPHAD method enables unknown thermodynamic properties and phase equilibria of multicomponent systems to be predicted. Credibility criteria have been defined to indicate the confidence that may be placed in any given phase diagram calculation:
  - FAB: fraction of fully assessed subcomponent binaries;
  - FAT: fraction of fully assessed subcomponent ternaries.
- Examples using the CALPHAD method to anticipate the formation of microstructures in precipitation-strengthened FCC-based HEAs:

- Phase equilibria:
  - Global computing approach: equilibrium proportions, compositions of stable phases at fixed compositions and temperature with discrete exploration and screening;
  - Precipitation strengthened FCC HEAs in the Al-Co-Cr-Fe-Ni-Ti system: guide for designing composition to obtain a specific microstructure.
- Phase transformations;
- Materials properties: yield strength, magnetic properties, stacking fault energy.

- Use of machine learning: the potential of using machine learning even with small datasets (less than 100 alloys) has been shown, as for example with the development of a machine learning model for high temperature oxidation resistant BCC-based Refractory high-entropy alloys (RHEAs) (Al-Cr-Mo-Nb-Ta-Ti-Zr).

Fabrication/manufacturing

The presentations in this session mainly addressed the manufacturing of HEAs, either in the form of films or as bulk materials, and their related microstructure and properties. The session was chaired by Yong Dai (PSI, Switzerland).

Francesco Fanicchia from the Welding Institute Ltd (TWI, United Kingdom) gave a presentation on the "Manufacturing of complex concentrated alloys (CCAs): Microstructure, performance and challenges". In fact, CCAs have been of great interest in recent years. CCAs can be manufactured using different techniques, such as solid-state manufacturing, liquid-state manufacturing, thin-film deposition and additive manufacturing. Materials properties and microstructure depend strongly on the manufacturing methods. In his presentation, some examples were detailed for materials prepared with different techniques:

- The grain size of CCAs can be controlled by the cooling rate (K/s) during manufacturing, e.g. by laser metal deposition (LMD), the cooling rate is in the range of 10^4 to 10^6 K/s, and gives grain sizes in the range of 100 nm to 10 µm.
- The grain morphology depends on the temperature gradient (G) and grain growth rate (R): high G and low R result in planar grain shape, while low G and high R induce an equiaxed dendritic structure.
- $CoCrFeMo_{0.85}Ni$ coatings were deposited on carbon steel by LMD and high velocity oxygen fuel spray (HVOF): the corrosion rate in 3.5% NaCl and sliding wear rate are much higher for the coatings prepared with HVOF. FCC structure was observed for the alloy prepared using LMD, while a mixed FCC and BCC structure was found for that prepared using HVOF.

Anna Fraczkiewicz (Mines Saint Etienne, France) gave a talk entitled "Design, fabrication and evaluation of Co-free austenitic HEAs", together with Jessica Delacroix (Aperam, France). The equiatomic CoCrFeMnNi HEA, also named Cantor alloy, is a single-phase FCC alloy with good mechanical resistance and high ductility, but cobalt is detrimental and unsuitable for nuclear applications. Based on the Cantor alloy, a Co-free HEAs (Y3) has been designed, then a CCA based on the Y3 grade was further developed. The R&D started with thermodynamics calculations (design). The alloys were then produced at laboratory scale. Evaluations at different levels are ongoing. The work is completed in close collaboration with industrial partners.

- Ingots of up to 2.5 kg were prepared for a Cantor alloy (equiatomic CoCrFeMnNi) and a non-equiatomic alloy, the A3S grade. The materials went through treatments: annealing at 1 000°C/2h, hot forging at 1 000°C, and cold rolling of 80%. Afterwards, the materials were characterised with various microstructural analysis and mechanical testing.
- In as-forged condition, the A3S alloy shows higher yield strength, but similar ductility as compared to the Cantor alloy. After annealing at 1 000°C, the compression test results for the both alloys are essentially the same.
- From the A3S grade, the Y3-grade ($Fe_{46}Cr_{15}Mn_{17}Ni_{22}$) was developed. In as-forged conditions, or annealed at < 660°C, the yield strength (YS) is about 500 MPa. After annealing at > 650°C, recrystallisation occurs and yield stress drops to ~250 MPa.
- The thermal stability of the alloys was verified by annealing at 500°C for 100-500 days. Some differences between the experimental results and the prediction of thermodynamics calculation were observed.
- A significant increase in the mechanical resistance (YS of 780 MPa at room temperature) could be obtained through the presence of secondary phases in Al and Ti alloyed Y3.
- Alloy production does not bring unsolved issues, the high content of Mn being the main difficulty. Thermomechanical processing is possible in "standard" conditions.
- A pre-industrial Y3 grade is being manufactured at Aperam, with controlled and increased level of impurities (O, C, N, P, S). The preliminary results show no detrimental effects of the impurities.

Phase stability, microstructural characterisation, mechanical testing

This session, chaired by Yong Dai from the Paul Scherrer Institute (PSI, Switzerland), included two presentations on the mechanical properties of HEAs in relation with their specific microstructure.

Edward J. Pickering (University of Manchester, United Kingdom) gave an overview of the microstructures and mechanical properties of HEAs. In general, the exceptional compositional diversity of HEAs results in very diverse microstructures and mechanical properties. Microstructures are normally very complex, while most mechanical properties seem to fall within conventional alloy performances.

- FCC HEAs (Cantor's alloys): in solid solutions, strength and ductility are improved by twinning-induced plasticity and transformation-induced plasticity.
- BCC/HCP RHEAs: some have good phase stability at high temperatures and show impressive high temperature strengths. But the ductility can be very limited at low temperatures.
- Superalloys HEA: often with BCC/B2 or FCC/L1 structures.
- Low-activation HEAs: V-Cr-Mn, V-Cr-Mn-Fe and V-Cr-Mn-Fe-Al_x alloys could be applied to fusion materials. Usually, they are rich in refractory elements since many of these elements are low-activation.

- Light-element HEAs: there are not many light elements to form light HEAs. Typical elements are Mn, Al, Li, Si, Ti, Sc, etc. The properties appear worse than conventional Al / Mg alloys.

Jean-Phillippe Couzinié (CNRS, France) addressed the mechanical properties and underlying deformation mechanisms of complex concentrated alloys. Published results in the open literature on active deformation mechanisms in HEA/CCAs were reviewed. He gave more specific insights into deformation mechanisms in refractory compositions:

- A comprehensive comparison of mechanical properties (typically tension and compression) between HEAs and conventional FCC/BCC alloys can be found in many publications, e.g. George, Curtin, Tasan, Acta Mat., 188, 435-474, 2020.
- For FCC-based HEAs, at low temperatures, twinning is the key deformation mechanism. At high temperatures, the overall mechanical behaviour of CrFeCoNi alloys is close to that of Ni-based superalloys.
- Refractory HEAs/CCAs, based on elements in the IV, V and VI columns (e.g. MoNbTa(V)W), show high strength above 800°C.
- Refractory CCAs often suffer from a lack of ductility, except for some HfNbTaTiZr-based alloys. The strategies for increasing the ductility are: (1) to design alloys with valence electron concentration below 4.5: single-phase alloys using only elements from subgroup IV-V; (2) to add Hf, Ti, Zr, which generally improve ductility, while subgroup V, VI elements and/or Al often improve strength, but reduce ductility.
- The local composition and core structure may play an important role in dislocation mobility in CCAs, which results in a strong temperature dependence of strength, ductility and deformation mechanisms.

Compatibility with corrosive environments

This session, chaired by Céline Cabet (CEA, France), Co-Chair of the EGISM, included two presentations addressing various environmental degradations of HEAs and of more recently proposed multi-principal entropy alloys (MPEAs): corrosion in liquid lead alloys, high temperature oxidation, aqueous corrosion and molten salt corrosion.

Alfons Weisenburger (KIT, Germany) presented two families of HEAs/CCAs specifically developed for their corrosion resistance starting from the alumina forming FeNiCrAl system. Alloys were first designed based on CALPHAD computations in FeNiCrAl + Nb, Ti, Cu for promoting single-phase FCC. Different compositions were tested in liquid lead. Nb was observed to promote a protective and adherent alumina scale. However, precipitation of secondary phases within the alloy was induced by corrosion due to Nb’s poor thermal stability.

This first generation of CCAs, together with alloys manufactured in the system FeNiCrAl + (Mn, Co) + (Zr, Y), were tested at 1 000-1 200°C in steam and oxygen. The effect of the various elements was identified through X-ray diffraction (XRD), thermogravimetric analysis (TGA) and cross-section examination: combining Co and Y was the most efficient way to limit high temperature oxidation. Beyond their promising corrosion properties, the deployment of these materials would require establishing their thermal and mechanical properties, and, for use under irradiation, testing their radiation tolerance.

Alloys were produced with a laboratory arc melter from pure elements and melted several times. The carbon content was not analysed, but it is assumed to be very low.

Pr. John R. Scully (University of Virginia, United States) discussed from a more theoretical stance the corrosion and passivation attributes of MPEAs mainly in aqueous solutions. The ambition is to clarify why some HEAs exhibit excellent resistance and others poor aqueous behaviour although they all contain beneficial elements such as Cr, Al, Nb, Ti, Ta and above the critical level for promoting passivation. A combinatorial approach has been used for Al+Cr [FeCoNi] with thin films sputtered on wafers and analysed before/after heat treatment by XRD and electrochemistry for finding single-phase FCC and duplex FCC+BCC compositions with good passivation properties. Larger ingots of alloys were then produced by arc melting and further investigated. Electrochemical techniques showed that the most protective oxide is a solid solution spinel of (Fe, Ni, Cr, Mn Co)3O4. The stability of each element in the spinel was later tracked by combining ex-situ and operando surface characterisation techniques and polarisation curves. High temperature oxidation only produces mixed oxides. However, third elements play an important role in the different oxide properties.

Corrosion in molten salt was only rapidly introduced. As a conclusion, high throughput modelling approaches were promoted to explore oxide formation, which is key to designing new corrosion resistant alloys.

Irradiation resistance

The presentations of this session, chaired by Jian Gan (INL, United States), addressed mainly the radiation tolerance of HEAs.

Flyura Djurabekova (University of Helsinki, Finland) detailed the identified mechanisms of radiation damage build-up in HEAs. Experiments conducted at ORNL have shown that damage in some FCC HEAs can be clearly lower than in the corresponding pure elements like Ni. However, single cascades in HEAs do not really show a difference to pure elements. A mechanistic understanding is needed to explain the difference on radiation damage. The simulation studies and Rutherford backscattering spectrometry (RBS)/Channelling experiment in this work revealed the following:

- Simulation results of a NiFe block with more than 1 500 overlapping cascades show that at about 0.05 dpa almost all damage is in clusters and evolves.
- The simulated clustered damage shows a similar damage reduction effect as the experiments.
- Dislocation structures are analysed by simulation including stacking fault tetrahedra (SFT), Shockley partials and Frank loops. Pure Ni has larger dislocation loops and much more SFTs than NiCoCr.
- Dislocations dominate the overall damage level and irradiation leads to numerous dislocation reactions. For example, Shockley partial can stepwise become a Frank loop.
- Simulation shows that the damage reduction in HEAs is clearly correlated to the reduced dislocation mobility. Lower mobility prevents dislocations from growing, and smaller dislocations can recombine relatively easily during cascade overlap.
- RBS/Channelling experiments showed a very high damage level at low dose, inconsistent with transmission electron microscopy (TEM), resistivity

measurement or molecular dynamics (MD) simulation. It is surmised that this may happen because the dislocations give a very high RBS/C signal due to strain effects. A new code to simulate RBS/C was developed to directly compare the defect structure with the experiment measurements without fitting.

- A machine-learned potential for 5-element BCC HEAs was developed and proved to be two orders of magnitudes faster than conventional Gaussian Approximation Potential approaches.
- Simulation for BCC HEA shows that the smallest atoms tend to segregate at the interstitial dislocation loops and the largest atoms tend to be enriched at the inner surface of voids. The dislocation size in pure tungsten is significantly larger than that in BCC HEA.

It can be concluded that dislocation mobility is reduced in HEAs as compared to constitutive elements, which may be responsible for reduced radiation damage. The size of radiation-induced defects in HEAs is smaller than in corresponding pure elements.

Regarding efforts to develop Cobalt-free HEAs for nuclear application, Naoyuki Hashimoto (Hokkaido University, Japan) presented the new results on the alloying effect on stacking fault energy (SFE) and radiation damage in Cobalt-free HEAs. An increase in the SFE can affect stacking fault formation and suppress irradiation hardening. FeCrNiMn was used as a Co-free HEA with comparison to CoCrFeNiMn. Irradiations were conducted with 1 MeV electrons at 400°C to 0.2 dpa and 8 MeV Au ions at 500°C to 73.2 dpa, and TEM characterisation was performed. This work showed the following results:

- SFE of FeCrNiMn seems to be dependent on the Ni+Mn content. SFE increases with increasing Ni+Mn for both CoCrFeNiMn and FeCrNiMn HEAs.
- The yield stress and elongation in $FeCr_{0.8}Ni_yMn_z$ increase with increasing Ni and Mn contents. The ultimate tensile strength (UTS) and elongation of $FeCr_{0.8}NiMn_{1.3}$ and $FeCr_{0.8}Ni_{1.3}Mn_{1.3}$ are significantly higher than those of 316H stainless steel.
- The effect of grain size on yield stress is less than the solid solution effect.
- Electron irradiation to 0.2 dpa shows that increasing Ni and Mn contents in $FeCr_{0.8}Ni_yMn_z$ decreases the Frank loop number density, but with no noticeable effect on the loop size. It shows increasing SFE would suppress the Frank loop formation.
- Au ion irradiation up to 73.2 dpa shows no void formation in $FeCr_{0.8}Ni_yMn_z$ HEAs.

It can be concluded that good mechanical properties and radiation resistance can be achieved in Co-free HEAs by optimising the Ni and Mn content in order to increase the SFE in $FeCr_{0.8}Ni_yMn_z$ HEAs. A higher SFE will suppress the formation of Frank loops.

Shijun Zhao (City University of Hong Kong) presented the theoretical modelling of irradiation resistance in HEAs or MPEAs. In his presentation, the defect production, formation, diffusion, recombination and interactions were addressed. This work showed the following results:

- MD simulation confirms that Ni, NiFe, $Ni_{0.8}Cr_{0.2}$ and $Ni_{0.4}Fe_{0.4}Cr_{0.2}$ have a similar atomic displacement threshold energy E_d.
- MPEAs exhibit a higher vacancy formation energy vs. a lower interstitial formation energy.

- Stacking fault energies govern the formation of dislocations. The distribution of SFEs can be correlated with electronic density and is significantly wider in MPEAs than in pure element.
- MPEAs display higher interstitial migration energy vs. lower vacancy migration energy. A strong chemical effect is observed on the defect migration energy.
- MD simulation shows that smaller clusters migrate faster, whereas large clusters diffuse more slowly in MPEAs than in a pure metal. Defect evolution is delayed in MPEAs.
- Due to fluctuation in SFEs, a waving dislocation line can impede the dislocation motion in MPEAs, leading to higher threshold stress and slower dislocation velocity.
- The recombination volume of Frankel defects in NiFe is significantly increased due to chemical disorder. Substitution of Fe by Cr can further improve the recombination in $Ni_{0.5}Fe_{0.5-x}Cr_x$.
- Disorder induces significant fluctuations in the strain energy and stress field around the dislocation. Dislocation bias in NiFe is reduced as compared to pure Ni.
- Local ordering enhances the sink strength of grain boundaries for vacancies, but, at the same time, reduces the sink strength for interstitials.
- Site preference of helium is substantially reduced in MPEAs, leading to different binding properties. NiCoFeCr shows a weaker binding of He-V, and a stronger binding of He-V2.

In summary, irradiation damage in HEAs or MPEAs is lowered because (1) defect mobility is reduced, (2) the evolution of an extended defect is generally delayed, (3) defect recombination is enhanced, and (4) local fluctuations tend to screen defect interactions.

Conclusion: HEAs for nuclear applications - opportunities and limitations

The workshop concluded with a panel discussion, chaired by Prof. James Marrow (Oxford University, United Kingdom), on the applications, opportunities and limitations of HEAs for nuclear applications. It featured three panellists:

- Dr Francesco Fanicchia, Senior Project Leader, Surface Engineering (TWI Limited, United Kingdom);
- Dr Edward Pickering, Research Area Lead for the Advanced Metals Processing theme (Henry Royce Institute, University of Manchester, United Kingdom);
- Dr Yanwen Zhang, Distinguished R&D Staff (ORNL, and Department of Materials Science and Engineering at University of Tennessee, United States).

The discussion was shaped around a series of questions, on which the panel consensus is summarised. This forms the conclusion of the workshop.

What confidence do you have that there will be future applications of HEA?

There is confidence in future applications, and the drive for their development comes from the end users. The applicability is higher for the broader range of multicomponent alloys (not strictly HEAs) than the more exotic alloys with low TRL. Useful alloys are already being found in the compositional space that is quite close to conventional alloys, and there are already commercially available HEAs in non-nuclear fields (e.g. brazing alloys), though there is a further need to explore the huge compositional space that is available.

In what types of components and in what systems do you foresee HEAs being used?

They would generally need to be applications where there are currently no solutions. Since these alloys have high costs and the processing is not optimised, the applications need to be in high value components. Nuclear energy is a good example of this. For instance, fusion energy needs alloys for the plasma-facing components of the breeder blanket; the tungsten divertor would be expected to be a more challenging application as tungsten generally becomes more brittle with alloying. The palette of alloying elements in fusion is restricted somewhat due to low-activation requirements. This is challenging as many HEAs include Nb as a stabilising element for FCC structures. In Generation IV systems, such as molten salt reactors, there are opportunities to optimise surface alloys for corrosion resistance and functionalisation to affect reaction products to outperform stainless steels.

What are the key challenges and opportunities in the manufacturing methods required for HEAs?

After designing an alloy, manufacturing is a real challenge, as is predicting the alloy microstructure evolution and properties achieved after manufacturing, especially with the introduction and control of impurities. In addition to the effects of interstitial impurities on properties (e.g. in BCC HEA), one needs a broad composition space where the phases are stable. Cost is an issue for bulk alloys, so coatings on conventional alloys can reduce the cost of manufacturing and materials. Therefore, additive manufacturing is an exciting opportunity.

What are the main stages and challenges to the qualification of HEAs for nuclear applications?

The challenges are the same as with any new alloy. Similar to aerospace, the costs of qualification testing are high, and one needs cost effective techniques otherwise one cannot test all compositions, particularly as one moves to higher TRL. For nuclear, obtaining properties following irradiation will be difficult due to the very significant costs of neutron irradiations and the lack of availability of fusion-relevant conditions (14 MeV neutrons). It is possible that "normal" qualification will not be done for fusion applications, and this will require informed interaction with regulators.

What is the need for irradiation data (and of what type), and is it available?

Ion irradiation can be used to investigate the effects of irradiation, but the differences between ion and neutron irradiation in concentrated alloys such as HEAs are significant, and need to be addressed with improved modelling tools (including electronic energy deposition and the validity of surface-limited ion damage at high temperatures). There are some novel developments with sequential neutron and ion irradiations to accelerate damage and address the lack of availability of 14 MeV fusion-relevant facilities.

What are the likely timescales for the implementation of HEAs in advanced nuclear systems?

Tools such as machine learning might shorten the time to identify new HEAs, and the aerospace industry generally takes five years to bring a new alloy into service; but this industry has substantial experience in new alloys with small changes in their compositions. Therefore, the expected timescale for HEAs will be longer for nuclear applications. This could be shortened with significant effort if there is high confidence in a given alloy and a willingness to invest in its development.

How can progress be accelerated?

New alloys may be found and developed more quickly by exploring the compositional space around the already well-understood systems. To accelerate progress, dialogue is needed between the HEA and conventional alloy communities, with critical comparisons between the new alloys and conventional systems, from which much can be learnt.