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Editorial

Special Issue "Advanced Refractory Alloys": Metals, MDPI

Oleg N. Senkov [1,*], Panagiotis (Panos) Tsakiropoulos [2] and Jean-Philippe Couzinié [3]

1 Air Force Research Laboratory, Materials and Manufacturing Directorate, Wright-Patterson AFB, OH 45433, USA
2 Department of Materials Science and Engineering, Faculty of Engineering, Sir Robert Hadfield Building, The University of Sheffield, Mappin Street, Sheffield S1 3JD, UK; p.tsakiropoulos@sheffield.ac.uk
3 Université Paris Est Créteil, CNRS, ICMPE, UMR7182, F-94320 Thiais, France; couzinie@icmpe.cnrs.fr
* Correspondence: oleg.senkov.ctr@us.af.mil

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Metallic materials with extreme and often unusual combinations of properties are always in high demand in the competitive world market. Current state-of-the-art metallic materials, such as Ni-based superalloys, are approaching the physical limits of their development, as the operating temperatures required for future applications are close to or beyond their melting points. Progress in high social-impact fields, such as energy and transportation, requires the exploration and development of new material solutions with improved structural or functional properties at much higher temperatures.

Advanced refractory alloys—in particular, refractory intermetallic composites (RMICs) such as Nb-silicide in situ composites, Mo-silicide based alloys, refractory high-entropy alloys (RHEAs), refractory complex concentrated alloys (RCCAs), and refractory superalloys (RSA)—attract a great deal of attention as potential structural materials for use at temperatures far beyond those possible with Ni-based superalloys [1–5]. The remarkable properties of some of these alloys make them promising candidates for use in a wide range of current and future applications. These advanced materials are based on 13 refractory metals, W, Re, Os, Ta, Mo, Nb, Ir, Ru, Hf, Rh, V, Cr, and Zr, whose melting points are between 1855 °C (Zr) and 3422 °C (W). They may also contain other elements such as Al, Si, and Ti, aiming at improving design-required properties (mechanical and/or environmental, mainly).

The properties of refractory metals belonging to different groups in the periodic table vary significantly. The common characteristics of refractory metals and their alloys are a high melting point, high strength at high temperatures, and good corrosion resistance to liquid metals. Partly due to their high melting point, refractory metals are stable against creep deformation up to very high temperatures. Refractory metals can be worked into wires, ingots, rebar, sheets, or foil. They are used in a wide range of applications, including hot metalworking, furnaces, lighting, lubricants, nuclear reaction control rods, chemical reaction vessels, and space nuclear power systems. They are also key high-temperature materials used for aerospace applications. Furthermore, refractory metals are used as alloying additions—for example, in steels, superalloys, and high-entropy alloys (HEAs). Finally, it should be mentioned that most refractory metals are biocompatible, paving the way toward the development of biomaterials for use in implant applications. Poor low-temperature fabricability and poor oxidation at high temperatures are shortcomings of most refractory metals and alloys. Oxidation can be improved through the use of specific combinations of refractory metals and alloying additions. Interactions with the environment can significantly influence their high-temperature creep strength. The application of these metals and alloys at high temperatures often requires the use of a protective atmosphere or coating.

Lately, RMICs, RHEAs, RCCAs, and RSAs have been the subject of intense investigations, many of which relate to the design of new ultra-high-temperature materials for aerospace applications. The papers published in this Special Issue provide new information on the development, properties, and possible applications of these groups of advanced refractory alloys. The results reported in these papers are briefly outlined below.

The paper by Shuaidan Lu et al. [6] studies how V and Ti additions affect the oxidation behavior of WMoTaNb RHEA at 1000 °C. The reported results clearly indicate that the additions of V and Ti do not improve the resistance of WMoTaNb. In particular, the effect of V is harmful to the overall behavior, as it tends to deteriorate the oxide volatility, leading to dramatic internal oxidation.

Nikos Vellios et al. [7] discuss the microstructure, oxidation, and hardness of an RMIC based on Nb—i.e., a RM(Nb)IC—with Sn, Ti, and V additions and a high-volume fraction of Nb solid solution. The Nb-rich solid solution (Nbss), αNb_5Si_3, γNb_5Si_3, and HfO_2 phases were present in the as-cast or heat-treated alloy plus TiN in the near-the-surface areas of the latter. The vol.% of Nbss was about 80%. The V partitioned to the Nbss, where the solubilities of Al, Cr, Hf, and V increased with increasing Ti concentration. At 700, 800 and 900 °C, the alloy did not suffer from catastrophic pest oxidation; it followed parabolic oxidation kinetics in the former two temperatures and linear oxidation kinetics in the latter, where its mass change was the lowest compared with other Sn-containing alloys. A Sn-rich layer formed in the interface between the scale and the substrate, which consisted of the Nb_3Sn and Nb_6Sn_5 compounds at 900 °C. The latter compound was not contaminated with oxygen. Both the Nbss and Nb_5Si_3 were contaminated with oxygen, with the former contaminated more severely than the latter. The bulk of the alloy was also contaminated with oxygen. The alloying of the Nbss with Sn increased its elastic modulus compared with Sn-free solid solutions. The hardness of the alloy, its Nbss, and its specific room temperature strength compared favorably with the properties of many refractory metal-complex-concentrated alloys (RCCAs).

RSAs have been heralded as potential new high-temperature structural materials. They have nanoscale cuboidal BCC+B2 microstructures that are thought to form upon quenching through a spinodal decomposition process driven by Ta-Zr or Nb-Zr miscibility gaps, followed by the ordering of one of the bcc phases. However, it is difficult to isolate the role of different elemental interactions within compositionally complex RSAs. In their manuscript, Tamsin E. Whitfield et al. [8] investigated the microstructures produced by the Nb-Zr miscibility gap within the compositionally simpler Ti-Nb-Zr constituent system. They studied a systematic series of alloys with compositions of $Ti_5Nb_xZr_{95-x}$ (x = 25–85 at.%) following quenching from solution heat treatment and long duration thermal exposures at 1000, 900 and 700 °C for 1000 h. During exposures at 900 °C and above, the alloys had a single bcc crystal structure. At 700 °C, alloys with 40–75 at.% Nb contained three-phases BCC1, BCC2 and HCP, and a large misfit, 4.7–5%, was present between the lattice parameters of two bcc phases. Evidence of nanoscale cuboidal microstructures was not observed, even in slow-cooled samples. Whilst it was not possible to conclusively determine whether a spinodal decomposition occurs within this ternary system, these insights suggest that Nb–Zr interactions may not play a significant role in the formation of nanoscale cuboidal RSA microstructures during cooling.

In their paper, Senkov et al. [9] offer a multi-scale study on the effect of Re on the microstructures, phase compositions, and mechanical properties of NbTiZr and TaTiZr ternary alloys. The addition of Re is an efficient way to improve the ductility of initially brittle refractory alloys and leads to a significant enhancement of high-temperature strength. Here, the authors highlight that Re additions have interesting effects on the mechanical properties of NbTiZr in the RT–1200 °C temperature range. Re causes the formation of an FCC Laves phase in the BCC matrix and induces a significant reduction in the alloy grain size. In TaTiZr, the effect of Re is two-fold: in addition to a slight increase in the strength, the Re addition considerably improves the ductility in the RT–1200 °C range. Strengthening processes as well as comparisons between observed microstructures and Calphad predictions are discussed in this paper.

Maximilian Regenberg et al. [10] reported on the biocompatibility of an equiatomic Nb-Ta-Ti alloy, which they used as the basis for the development of a novel, biomedical, multicomponent alloy. The alloy was produced by arc melting and its biomedical properties were compared with the properties of elemental Ta and Nb, alloy Co-28Cr-6Mo, and alloy Ti-6Al-4V. The biocompatibility of the novel alloy Nb-Ta-Ti was evaluated by means of cell (osteoblast) attachment as well as monocyte inflammatory response analysis. The results indicate competitive osteoblast attachment, as well as comparable expressions of fibrosis markers in comparison to conventionally used biomedical materials. In addition, the Nb-Ta-Ti alloy showed a markedly reduced inflammatory capacity, indicating its high potential for use as a prospective biomedical material.

Gengbiao Chen et al. [11] studied the effect of Zr additions on the microstructure, mechanical properties, and wear resistance of $MoNbTiZr_x$ (X = 0, 0.5, 1) RHEAs, which were prepared by vacuum arc melting. All three alloys had a single BCC phase. The $MoNbTiZr_{0.5}$ alloy exhibited the smallest grain size, highest room temperature compression strength, and the best wear resistance, with a friction coefficient of about 0.33. It also displayed the widest wear scar, the shallowest depth, and the greatest degree of wear on the grinding ball because of the formation of an oxide film during wear.

Petra Pfizenmaier et al. [12] reported the tensile creep behavior of a binary alloy $Cr_{91}Si_9$ and two ternary alloys, $Cr_{91}Si_7Ge_2$ and $Cr_{91}Si_7Mo_2$, in air at 980 °C. The tests were conducted under constant stress conditions of 50, 75, and 100 MPa. The substitution of Si with 2 at.% Ge or Mo considerably improved the creep resistance, with the highest resistance achieved by the alloy with Mo. A time- and load-dependent nitrogen effect was also observed. After longer exposures in air under the lowest applied stress (50 MPa), internal nitridation was observed to increase the creep resistance of these alloys. In this regime, compression stresses were induced along grain boundaries or at the crack tips of internal cleavage by the formation of Cr_2N precipitates. On the other hand, the time to failure was strongly reduced at higher stresses due to embrittlement.

Bin Hu et al. [13] investigated the high cycle fatigue properties of refractory metals containing single-crystal Ni-based superalloy at 800 °C. The study particularly focused on the influence of an orientation deviation (10–15°) around the <111> growth axis on the fatigue behavior. The results show that the deviation near <111> has a clear but negative influence on the fatigue life. The degradation of the behavior is highly dependent on the deviation direction of the single crystals—i.e., towards <100> or <110>— which greatly affects the nature of activated slip systems.

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References

1. Tsakiropoulos, P. Alloys for application at ultra-high temperatures: Nb-silicide in situ composites: Challenges, breakthroughs and opportunities. *Prog. Mater. Sci.* **2022**, *123*, 100714. [CrossRef]
2. Tsakiropoulos, P. *Beyond Nickel Based Superalloys, Encyclopedia of Aerospace Engineering*; John Wiley & Sons, Ltd.: Chichester, UK, 2010.
3. Senkov, O.N.; Miracle, D.B.; Chaput, K.J.; Couzinie, J.-P. Development and exploration of refractory high entropy alloys: A review. *J. Mater. Res.* **2018**, *33*, 3092–3128. [CrossRef]
4. Miracle, D.B.; Tsai, M.-H.; Senkov, O.N.; Soni, V.; Banerjee, R. Refractory high entropy superalloys (RSAs). *Scr. Mater.* **2020**, *187*, 445–452. [CrossRef]
5. Senkov, O.N.; Isheim, D.; Seidman, D.N.; Pilchak, A.L. Development of a Refractory High Entropy Superalloy. *Entropy* **2016**, *18*, 102. [CrossRef]
6. Lu, S.; Li, X.; Liang, X.; Yang, W.; Chen, J. Effect of V and Ti on the oxidation resistance of WMoTaNb refractory high-entropy alloy at high temperatures. *Metals* **2022**, *12*, 41. [CrossRef]
7. Vellios, N.; Keating, P.; Tsakiropoulos, P. On the microstructure and properties of the Nb-23Ti-5Si-5Al-5Hf-5V-2Cr-2Sn (at.%) silicide-based alloy—RM(Nb)IC. *Metals* **2021**, *11*, 1868. [CrossRef]

8. Whitfield, T.E.; Wise, G.J.; Pickering, E.J.; Stone, H.J.; Jones, N.G. An investigation of the miscibility gap controlling phase formation in refractory metal high entropy superalloys via the Ti-Nb-Zr constituent system. *Metals* **2021**, *11*, 1244. [CrossRef]
9. Senkov, O.N.; Gorsse, S.; Wheeler, R.; Payton, E.J.; Miracle, D.B. Effect of Re on the microstructure and mechanical properties of NbTiZr and TaTiZr equiatomic alloys. *Metals* **2021**, *11*, 1819. [CrossRef]
10. Regenberg, M.; Schmelzer, J.; Hasemann, G.; Bertrand, J.; Krüger, M. A novel alloy development approach: Biomedical equiatomic Ta-Nb-Ti alloy. *Metals* **2021**, *11*, 1778. [CrossRef]
11. Chen, G.; Xiao, Y.; Ji, X.; Liang, X.; Hu, Y.; Cai, Z.; Liu, J.; Tong, Y. Effects of Zr content on the microstructure and performance of TiMoNbZrx high-entropy alloys. *Metals* **2021**, *11*, 1315. [CrossRef]
12. Pfizenmaier, P.; Ulrich, A.S.; Galetz, M.C.; Glatzel, U. Tensile creep properties of Cr-Si Alloys at 980 °C in air—Influence of Ge and Mo addition. *Metals* **2021**, *11*, 1072. [CrossRef]
13. Hu, B.; Pei, Y.; Gong, S.; Li, S. Orientation dependence of high cycle fatigue behavior of a <111> oriented single-crystal nickel-based superalloy. *Metals* **2021**, *11*, 1248. [CrossRef]