

# Advances in Zr-Based Alloys

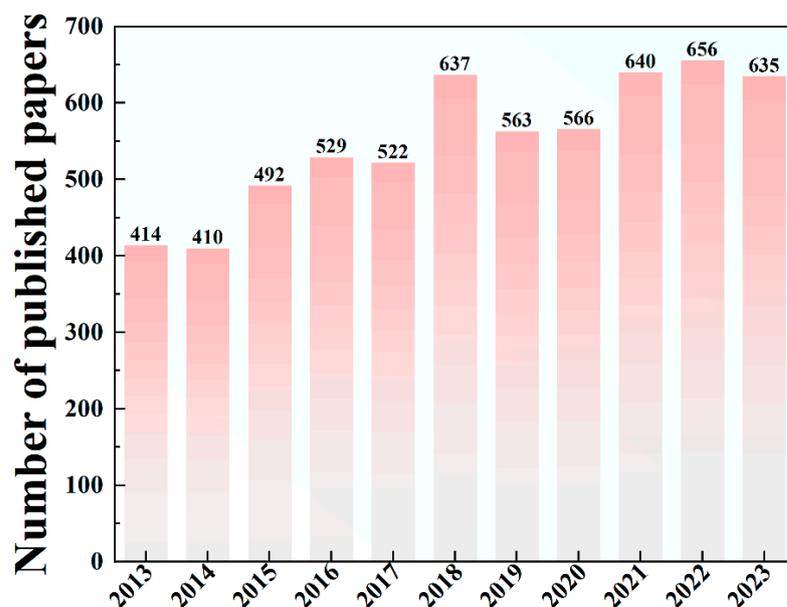
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Due to outstanding mechanical properties [1–4], good anti-neutron irradiation resistance [5–9], superior corrosion resistance properties [10–13], good biocompatibility [14–16], and so forth, zirconium (Zr) and its alloys have important application potential in the fields of nuclear technologies, aerospace, chemical research, biomedical industries, etc. [17]. However, as the needs of various industries continue to change, higher performance requirements have been put forward for Zr alloys. Therefore, advanced high-performance Zr alloys need to be designed, developed, and optimized to meet this demand.

An improved understanding of related research fields can be quickly obtained using bibliometric analyses [18–20]. To conduct an analysis of the research status on Zr alloys, relevant papers pertaining to Zr alloys published in the last 10 years were retrieved using the Web of Science Core Collection. The search employed Zirconium alloy as its subject term. A total of 6268 papers were identified, selected, and subsequently downloaded for in-depth analysis. Utilizing the retrieved data, Figure 1 presents an analysis of the quantity of publications about Zr alloys in the last 10 years. The observed trend in the number of published papers indicates a consistent upward trajectory, with the recent three years maintaining a count exceeding 600 papers. This observation underscores the significance of Zr alloys as a focal point within the broader field of materials science.



**Figure 1.** Number of publications published on Zr alloys in the Web of Science Core Collection in the last 10 years.

Furthermore, based on these bibliometric results, the research focus on Zr alloys was analyzed. Figure 2 depicts a network visualization of keywords that appear more



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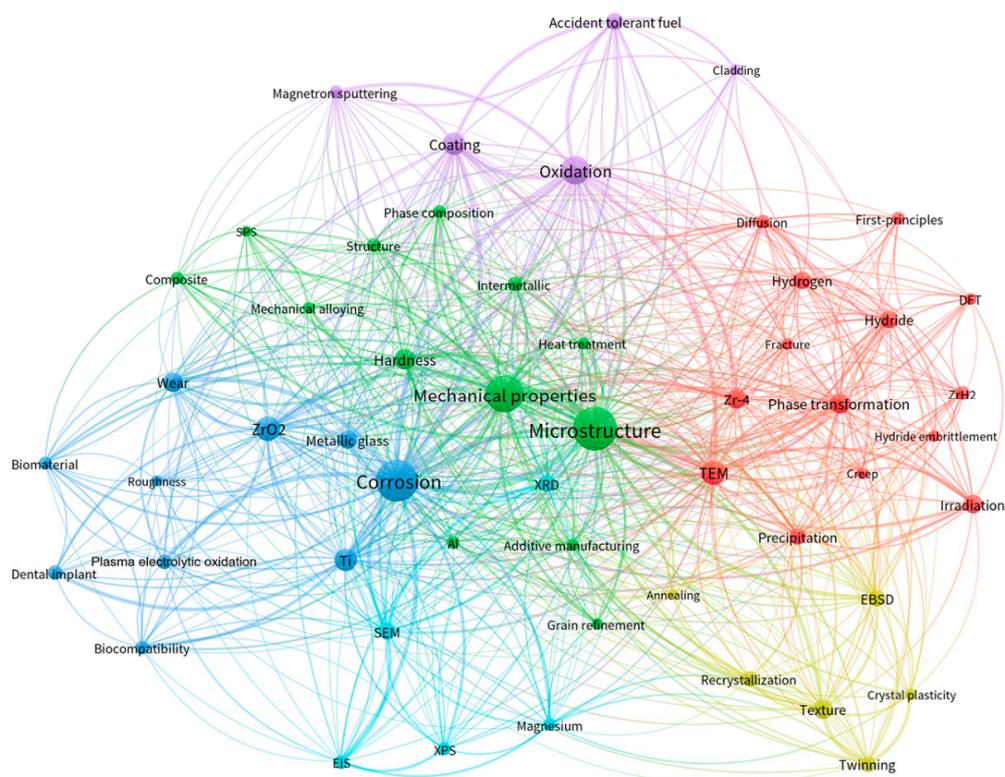
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than 40 times in papers related to Zr alloys over the last decade. The size of each circle corresponds to the frequency of keyword usage. Notably, prominent keywords such as “microstructure”, “corrosion”, “mechanical properties”, “oxidation”, “TEM”, “Ti”, “coating”, “ZrO<sub>2</sub>”, “hardness”, “phase transformation”, “SEM”, “texture”, “hydride”, “Hydrogen”, and “wear” rank among the top fifteen, signifying their central importance in the study of Zr alloys. Similarly, the colors of the circles indicate the relevance of the keywords, with each color representing a different cluster that may represent a given research direction. According to the color clustering of the keywords in Figure 2, several research directions on Zr alloys in recent years can be roughly summarized: (1) Research on the microstructure and mechanical properties of Zr alloys. (2) Research on the corrosion, wear, and protection of Zr alloys. (3) The oxidation and surface engineering of these alloys. (4) The characterization of recrystallization, texture, twinning, etc. (5). Experimental and computational simulations of phase transformation, precipitation behavior, and failure caused by hydrogenation, irradiation, creep, etc.



**Figure 2.** Network visualization of different keywords appearing no less than 40 times in the literature related to the term “Zirconium alloy” as published in the Web of Science Core Collection in the last 10 years.

Mechanical properties are one of the basic performance requirements of Zr alloys as a structural material, and the alloying [21–26] and processing [21,26–28] (including rolling, heat treatment, etc.) of Zr are extremely effective methods for modulating the material’s microstructure and improving its mechanical properties. The effect of Al content on the Zr’s mechanical properties and strengthening mechanisms has been thoroughly investigated by Wu et al. [29]. Al addition leads to grain size reduction and a Zr<sub>5</sub>Co<sub>7</sub>Al<sub>3</sub> intermetallic precipitation, and the best combination of mechanical properties (UTS and UFS of 464 MPa and 3.4%, respectively) was achieved for Zr<sub>47.5</sub>Co<sub>47.5</sub>Al<sub>5</sub> which demonstrated strong synergistic effects of fine grain strengthening, the solid-solution-strengthening of Al elements, and secondary-phase precipitation strengthening. Liu et al. [30] improved the mechanical properties of the new Zr-Ti-8V alloy through hot-rolling and annealing treatments and examined the effects of annealing temperatures. The phase composition

and mechanical properties of the rolled Zr-Ti-8V alloy were sensitive to the annealing temperature, i.e., many more fine needle-like  $\alpha$  phases were precipitated after annealing at 450 °C and the alloy exhibited the best strength–plastic ratio (1039 MPa, 8.2%). The dual-phase alloy with  $\alpha+\beta$  had higher hardness and wear resistance; however, the opposite trend was observed for the single  $\beta$ -phase alloy. Furthermore, the anisotropic mechanical behavior and associated microstructure evolution in annealed Zr-4 were investigated at room temperature by Sun et al. [31]. The basal  $\langle a \rangle$  slips were activated in the N ( $40^\circ$ – $50^\circ$ ) TB and TB orientation grains when loading along the RD, and the second-order pyramidal slips were activated in the grains when loading along the TD, leading to the anisotropic mechanical behavior of Zr-4 alloy.

The oxidation and microstructure stability of these alloys at high temperatures are the two main issues for their high-temperature applications. Surface modification technology is considered an effective means to improve the oxidation resistance of Zr alloys [32–36]. Wen et al. [37] investigated the oxidation behavior of FeCoNiCrMo high-entropy coatings by atmospheric plasma spraying on Zr-4 in steam at 1100 °C. A dense  $\text{Cr}_2\text{O}_3$  oxide layer was formed on the coating's surface after oxidation at 1100 °C, which grew from 1.5 to 3  $\mu\text{m}$  after 15 to 60 min of oxidation, and the FeCoNiCrMo high-entropy coatings and the substrates diffused simultaneously, the FeCoNiCrMo high-entropy coating can effectively delay the oxidation of the Zr-4 substrate. Zahra et al. [38] investigated the phase equilibria in the Ti-Al-Zr system at 1000–1300 °C via experimentation. The phase equilibria at all temperatures are different from the ones established before, i.e., B2-ordered  $\beta_0$  already exists at 1000 °C and remains stable up to at least 1300 °C and only traces of  $\text{Zr}_5\text{Al}_3$  were observed. The phase equilibria between  $\beta$ -Ti, Zr/ $\beta_0$ , TiAl, and  $\text{ZrAl}_2$  were determined at all temperatures.

Computer simulation of the irradiation effect in nuclear material is an important method for understanding its performance [39–43]. Pan et al. [44] investigated the trapping capability of small-vacancy clusters (two/three vacancies, V2/V3) in the  $\alpha$ -Zr doped with alloying elements (Sn, Fe, Cr, and Nb) via first-principle calculations. The alloying elements of Sn and Nb in the second site and Cr in the first site are more easily trapped by two vacancies in the supercells of  $\alpha$ -Zr containing 142-Zr atoms, respectively. The alloying elements of Sn in the third vacant site, Fe in the first vacant site, and Cr and Nb in the second vacant site are more easily trapped by three vacancies in the supercells of  $\alpha$ -Zr containing 141-Zr atoms, respectively.

Zirconia-based materials are widely used in nuclear energy engineering, engines, the biomedical field, power industries, etc., due to their outstanding chemical and radiation stability, as well as remarkable mechanical properties, such as high hardness, high strength, high fracture toughness, wear resistance, etc. [45–49]. Furthermore, the type and concentration of stable oxides significantly impact the structure, phase composition, and mechanical properties of some partially stabilized zirconia single crystals. Borik et al. [50] studied the phase composition, local structure, and mechanical characteristics of  $\text{ZrO}_2$  crystals partially stabilized with  $\text{Y}_2\text{O}_3$  and co-doped with  $\text{Nd}_2\text{O}_3$ ,  $\text{CeO}_2$ ,  $\text{Er}_2\text{O}_3$ ,  $\text{Tb}_2\text{O}_3$ , and  $\text{Yb}_2\text{O}_3$ . The phase composition and structure of crystals at the same total concentration of doping oxides depends on the degree of substitution of  $\text{Y}^{3+}$  cations by rare-earth cations, and the rare earth ions of the beginning of the lanthanide series predominantly occupy positions in the non-transformable tetragonal phase of crystals based on zirconium dioxide. The fracture toughness increases with an increase in the ionic radius of the rare earth element of the co-doped oxide, while the microhardness values of the crystals slightly decrease.

The present Special Issue on “Advances in Zr-Based Alloys” can be considered a status report reviewing the progress in Zr-based alloys that has been achieved over the past several years.

**Author Contributions:** All authors have read and agreed to the published version of the manuscript.

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