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Research progress of novel zirconium alloys with high strength and toughness

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Abstract

Atoms of zirconium (Zr) are often known as "first metals of the atomic age". Because of its low cross section for thermal neutron absorption, excellent corrosion resistance, and good mechanical and processing properties, it is extensively used in the nuclear industry. As the properties requirements of materials in chemical, medical and aerospace fields turn out to be higher, the application of Zr alloys in these non-nuclear fields has become more and more widespread due to their excellent properties. In addition to having a high melting point, Zr alloys also have a high specific strength and low thermal expansion coefficient. Therefore, Zr alloys have a very promising application in corrosion-resistant structural materials. This paper mainly introduces the development status of Zr alloys, the design and optimization of Zr alloy compositions, the mechanism of Zr alloy toughening and the prospects of Zr alloy applications in various fields.

With the rapid development of chemical, aerospace and maritime industry, traditional alloy materials can no longer meet the increasingly demanding service conditions, so scientists began to gradually shift the focus of research to other light metal materials (such as Al-based, Ti-based, Zr-based and other alloy materials) 0. The low thermal neutron absorption area (0.18×10^{-28} m^2) and the excellent corrosion resistance of Zr elements open up a broad prospect for the application of Zr and its alloys in specific fields such as nuclear industry and aerospace. The excellent corrosion resistance of Zr and its alloys in most acids, alkalis, and molten salts makes them a commonly used structural material in the chemical industry 0. Comparing Zr atoms with traditional alloying elements, Zr atoms demonstrate low density, low thermal expansion coefficient, and excellent biocompatibility. Therefore, Zr and Zr alloys are not only used as structural materials in the nuclear and chemical industries, but also in the medical field due to their non-magnetic properties, low modulus of elasticity, corrosion resistance and biocompatibility 0.

This paper briefly describes the current development of new high-strength Zr alloys and the composition design and optimization of Zr alloys, highlights the toughening mechanism of Zr alloys and gives an outlook on the application prospects of new high-strength Zr alloys.

1. Current status of development of Zr alloys

The element Zr was first discovered in zirconite in 1789 by the German chemist M.H. Klaprothe, who named a new oxide "Zirconia". After the reduction of potassium metal (K), the reduction of high-purity Zr chloride ($ZrCl_4$) by pure Na and the extraction of Zr metal by thermal separation of iodide, in 1944, the Luxembourg scientist W. J. Kroll succeeded in developing a method for the mass production of ductile Zr by the reduction of $ZrCl_4$ by magnesium metal (Mg), which has led to the development of large-scale applications of Zr metal. At the beginning of the development of Zr alloys, they were mostly used in the nuclear industry 0. As the research on Zr alloys becomes more and more mature, the application of Zr alloys in aerospace, medical and chemical fields has become more and more widespread in recent years.

1.1 Zr alloy for nuclear

It is shown that the introduction of tin (Sn), tantalum (Ta) and niobium (Nb) in Zr alloys can effectively reduce the corrosion of the alloy by impurities in Zr sponge without seriously impairing the thermal neutron economy of Zr alloys. Among them, the Nb element directly participates in the formation of the second phase 0. The addition of Ta element makes the Zr-Ta alloy generate stable ZrO_2 and Ta_2O_5 passivation films in the corrosion solution to protect the alloy matrix. Sn, as the α-Zr phase stabilizing element, mainly exists in the zirconium alloy matrix in the form of solid solution atoms in the zirconium alloy. The average size of the second phase of the zirconium alloy will increase slightly with the increase of Sn content, and the corresponding influence corrosion resistance of alloys 0. As a result, Zr-tin alloys have been extensively studied for the production of fuel cladding tubes, control rod guide tubes, pressure tubes, component boxes, and some structural materials. Zr alloys for nuclear applications have been studied by scientists from various countries, among which Zr-2 and Zr-4 alloys have been applied 0. In addition to Zr-tin alloys, a wide range of Zr-niobium alloys has been developed by the former Soviet Union for use in nuclear power plants, among which Zr-2.5Nb alloys are widely used in reactors as pressure tubes and component box shell plates because of their high strength, excellent dimensional stability and corrosion resistance.

In recent years, to enhance the economic efficiency of nuclear energy, ensure nuclear reactor safety and reliability, and extend the useful life of nuclear materials, the nuclear industry has put forward more stringent requirements for Zr alloys in terms of corrosion resistance, high temperature mechanical properties and irradiation resistance 0. For this reason, several new nuclear Zr alloys have been successfully researched and developed in the United States, France, Japan, Russia, China and other countries. Among them, ZIRLO, E635 and M5 alloys have been successfully used in nuclear reactors. These alloys are dimensionally stable in the reactor, resistant to high temperature creep and irradiation, and have excellent performance under high temperature and pressure. Based on the nuclear Zr alloys developed by other countries, China has successfully developed the new high tenacity NZ8 alloy and E635 alloy 0. The NZ2 alloy is similar in composition to the MDA alloy, and the NZ8 alloy is similar in composition to the E635 alloy. Both alloys have good mechanical properties and corrosion resistance 0.

1.2 Corrosion-resistant Zr alloys

With the development of the chemical industry, Zr alloys are increasingly used in many highly corrosive equipment. Zr is a passivated metal with a dense oxide film that resists corrosion by most strong acids and alkalis as well as molten salts. However, it is not resistant to corrosive acids and other corrosive hazards (such as copper chloride and ferric chloride solution) 0. Zr alloys contain an oxide film on their surfaces which provides excellent corrosion resistance, the performance can also be improved by surface pretreatment 0. Hao *et al.* 0 used microarc oxidation technique to grow ceramic films in situ on the surface of Zr702 alloy in phosphate electrolyte system. Test results show that: after the micro-arc oxidation treatment, the corrosion potential of the alloy increases and the corrosion current density decreases, making corrosion resistance of the alloy after micro-arc oxidation greatly improved compared with that of the Zr alloy itself. Wei *et al.* 0 observed the oxidation behavior of Zr alloys and CrAl-coated Zr alloys at temperatures between 360°C and 1160°C and discovered that the oxidation resistance of the coated Zr alloys was significantly better than that of the Zr alloys themselves, and the substrate was almost not oxidized at 1060°C. This is because the CrAl coating forms a dense Al_2O_3 and Cr_2O_3 barrier during the oxidation process, which protects the substrate.

At present, the corrosion-resistant Zr alloys used in the chemical industry are mainly Zr702, Zr704, Zr705 and Zr706 alloys. The Zr702 alloy has a small amount of O, H and N, and its composition is close to that of pure Zr. It has high corrosion resistance, but low mechanical properties, mainly used in sulfuric acid media containing $FeCl_3$, as a chemical pipeline. A Zr-niobium alloy, Zr705 is twice as strong as Zr702 in terms of mechanical strength, which is mainly used in chemical equipment such as fence heat exchangers, and requires high strength and elongation.

1.3 Biomedical Zr alloy

Biomedical alloys are an integral part of biomedical materials and are utilized widely in the treatment, replacement and repair of hard tissues such as teeth, joints and bones. They are more demanding and should have a smaller application range, smaller specifications and higher performance compared to traditional alloys 0. As bio-implant materials, biomedical alloys should have good biocompatibility and mechanical compatibility, as well as excellent corrosion resistance. Zr alloys are valued by researchers for their good biocompatibility, excellent corrosion resistance and low magnetization rate. Studies have shown that Zr alloy as a biomedical alloy material has no adverse effects on human body 0. The research on Zr alloys as biomedical materials started in the 1990s with the development of Zr-Ti-Nb alloy by Smith & Nephew Richards, which has the advantages of low modulus of elasticity and good biocompatibility, which started the research on biomedical Zr alloys 0. Williams *et al.* 0 confirmed experimentally that the alloy does have good resistance but low strength. Subsequent research scholars found that alloying of Fe elements can enhance superelastic strain or the shape memory strain of Ti-Zr-Nb alloy 0. With the rapid development of technology, the development of biomedical Zr alloys has received more support. In 1995, Kobayashi *et al.* 0 first applied Zr-Ti alloy, a special material, to clinical medicine, and Zhang 0 refined the Zr-Ti alloy in the late 1990s. Then Zr alloys for medical applications have been developed, such as Zr-Mo type β-Zr alloys 0, Zr-Nb Zr alloys 0, Zr-Mo-Ti alloys 0, etc.

1.4 New high strength and toughness alloy

With the rapid development of modern industry, more and more extreme corrosive environments, materials need to cope with the increasingly harsh media environment, the requirements for material corrosion resistance is also increasingly high. In particular, structural materials serving in the marine environment and chemical industry must not only meet the requirements of low density and high strength mechanical properties, but also have better corrosion resistance to resist the more complex environmental erosion in the ocean. Therefore, the preparation of new high-strength and corrosion-resistant Zr-based alloys with enhanced performance to meet the higher demands of modern industry will contribute positively to the development and application of Zr alloys. Jing *et al.* 0, found that the alloy has the good corrosion resistance and best material properties when the Zr, Ti atomic ratio is 1:1, and its $\alpha+\beta/\beta$ phase transition point is about 630°C. Based on the binary Ti-Zr alloy, many researchers have conducted further studies. Ji *et al.* 0 found that the addition of Nb element to Ti50-Zr50 alloy improved the fracture toughness of the alloy, and also concluded that phase composition, microstructure, mechanical properties, and Nb content are correlated. Ding *et al.* 0 further improved the corrosion resistance as well as the surface wear resistance of Zr-titanium alloy by thermal oxidation treatment. The addition of Al element to Ti-Zr binary alloy can cause an increase in lamellar α thickness and the highest tensile strength of the prepared Ti-Zr-Al alloy was increased by 40% compared to Ti-Zr alloy 0.

At present, our researchers have developed a variety of new high-strength Zr alloys to cope with the increasingly severe corrosive environments, such as Zr-Ti alloy 0, Zr-Cr alloy 0, Zr-Al alloy 0, Zr-B alloy 0, Zr-Be alloy 0, Zr-Ta alloy 0, Zr-Ti-Al alloy 0, ZrTiAlV alloy 0, etc. Compared with pure Zr, the tensile strength of these Zr alloys is significantly improved, and the applications in the development of high-strength Zr alloys are vast. Figure 1 shows the toughness performance parameters of various crystalline and amorphous Zr alloys, most of which have good plastic toughness while maintaining high strength.

1.5 Amorphous Zr alloys

Zr metal can be used to prepare not only conventional crystalline alloys, but also amorphous alloys and amorphous composites. The typical bulk amorphous state is $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ bulk Zr-based amorphous alloy, also known as "Vit1" 0. Subsequently, the researchers developed the block ZrAlNiCu amorphous alloy and ZrAlCuAg system block amorphous alloy with excellent corrosion resistance, high strength, large elastic limit and low elastic modulus 0. Zr-based amorphous has a wide range of application prospects. According to Ming *et al*. [49], TiZr-based alloys can be effectively strengthened by crystallization-amorphous nanostructures through in situ tensile and compression experiments and finite element simulations. The currently developed prepared armor-piercing warhead 0, with self-sharpening properties similar to those of depleted uranium armor-piercing ammunition and promising to surpass them, is a promising and ideal material. Amorphous composites can effectively improve the lower ductility of amorphous alloys 0, and have great potential for applications in electronics, biotechnology, chemical and marine engineering.

2. Composition design and optimization of a new high strength Zr alloy

There are two isomers of pure Zr: α-phase and β-phase. The α-phase has HCP structure at room temperature and the β-phase has BCC structure at high temperature, and a large number of sub-stable phases exist such as the martensitic phase (α′ phase with hcp structure, α″ with rhombohedral structure), the ω-phase, and the face centered cubic phase (FCC) 0. In the composition design of new high-strength Zr alloys, higher strength alloys can be designed based on different structural isomers.

For single-phase disordered solid solution type Zr alloys, adding alloying elements can better control the phase content and mechanical properties 0. By alloying Zr with alloying elements, not only are the mechanical properties improved, but also the α-β phase transition temperature is affected. According to the effect of alloying elements on the temperature of phase transition temperature, they are classified into the following three categories: α-phase stable elements, β-phase stable elements and neutral elements. Among them, the temperature of phase transition can be raised by using α-phase stabilizing elements, increasing the size of α-phase region as well as its stability. Such as metallic elements Al and non-metallic elements C, N, O. The β-phase stabilizing element is the opposite of the α-phase stabilizing element, mainly including V, Nb, Mo and other metal elements. The addition of neutral elements can not influence the α-β phase transition temperature, and for Zr alloys, the common neutral addition element is Ti. Ti and Zr have similar crystal structure and physicochemical properties, and can form infinite solid solution, so TiZr-based alloys have good solid solution strengthening effect 0. Therefore, the current research direction of new high-strength Zr alloys should be based on TiZr as the matrix with reasonable proportion of Al, V, Cr and other alloying elements to achieve the purpose of high-strength alloys.

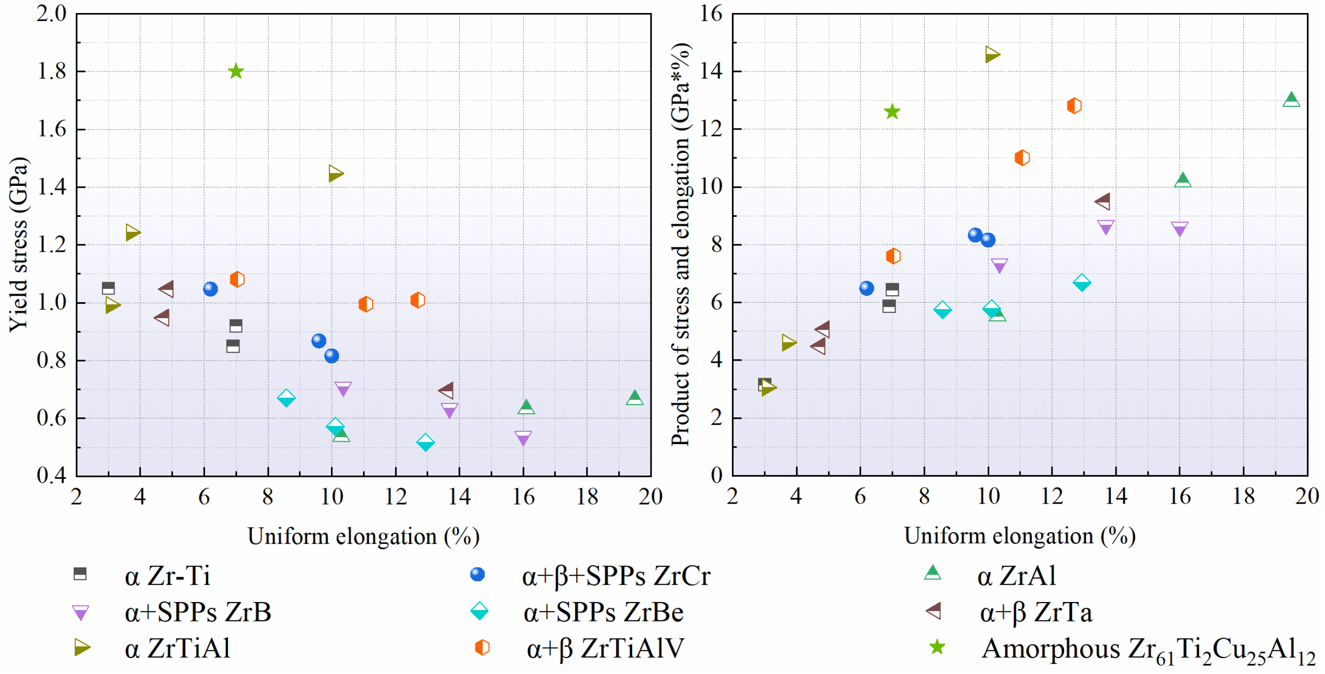

Figure 1. Summary of mechanical properties of crystalline and amorphous Zr alloys.

For duplex Zr alloys, the phase structure of the alloy will change, and the microstructure is rich, so researchers can optimize the alloy properties through microstructure design 0. On the one hand, the dual-phase Zr alloy includes α-phase and β-phase, which can make the alloy with certain plastic deformation ability; on the other hand, there are a great deal of α/β-phase interfaces in different forms of duplex organization, which contribute to strength. Therefore, according to the strengthening effect of the α/β-phase interface in the dual-phase structure and the strength design method, the Hall-Petch method was established for the strength design of dual-tough materials based on the toughness design of single-phase disordered solid solution Zr alloys, combining the influencing factors such as grain size, tissue morphology, defects and phase content of duplex Zr alloys 0. It is designed with different heat treatment process parameters to achieve the required properties of the duplex Zr alloy. A lot of Zr alloys have been designed and developed based on the Hall-Petch method (serval performance parameters of Zr alloys are shown in Table 1) 0. Compared with the conventional Zr-tin and Zr-niobium alloys for nuclear applications, the strength of the new high-strength Zr alloy has been increased by a factor of 1 to 5, without any reduction in plasticity.

Different heat treatment temperatures also affect the overall performance of the alloy. Zr alloys have a high melting point and high temperature solidification tends to lead to coarse and inhomogeneous structure, which greatly reduces the mechanical properties of Zr alloys. Therefore, a heat treatment process is needed to improve the properties of Zr alloys by regulating the organization of the alloy. As shown in Figure 2, the mechanical properties of ZrTiAlV alloys clearly rely on the annealing temperature and microstructure regulation 0. New high-strength Zr alloys generally use traditional heat deformation and heat treatment such as forging, hot rolling, annealing, solution aging, etc to optimize the microstructure of the alloy, enhance the strength of the alloy by tissue hyperfabrication and obtain good plasticity by tissue isotropization. Nowadays, a new way of optimizing the structure, compound deformation, has been applied to the preparation of Zr alloys. The design and optimization of the composition of the new high-strength Zr alloy requires consideration of various factors, but the ultimate goal is to improve the mechanical properties of the alloy.

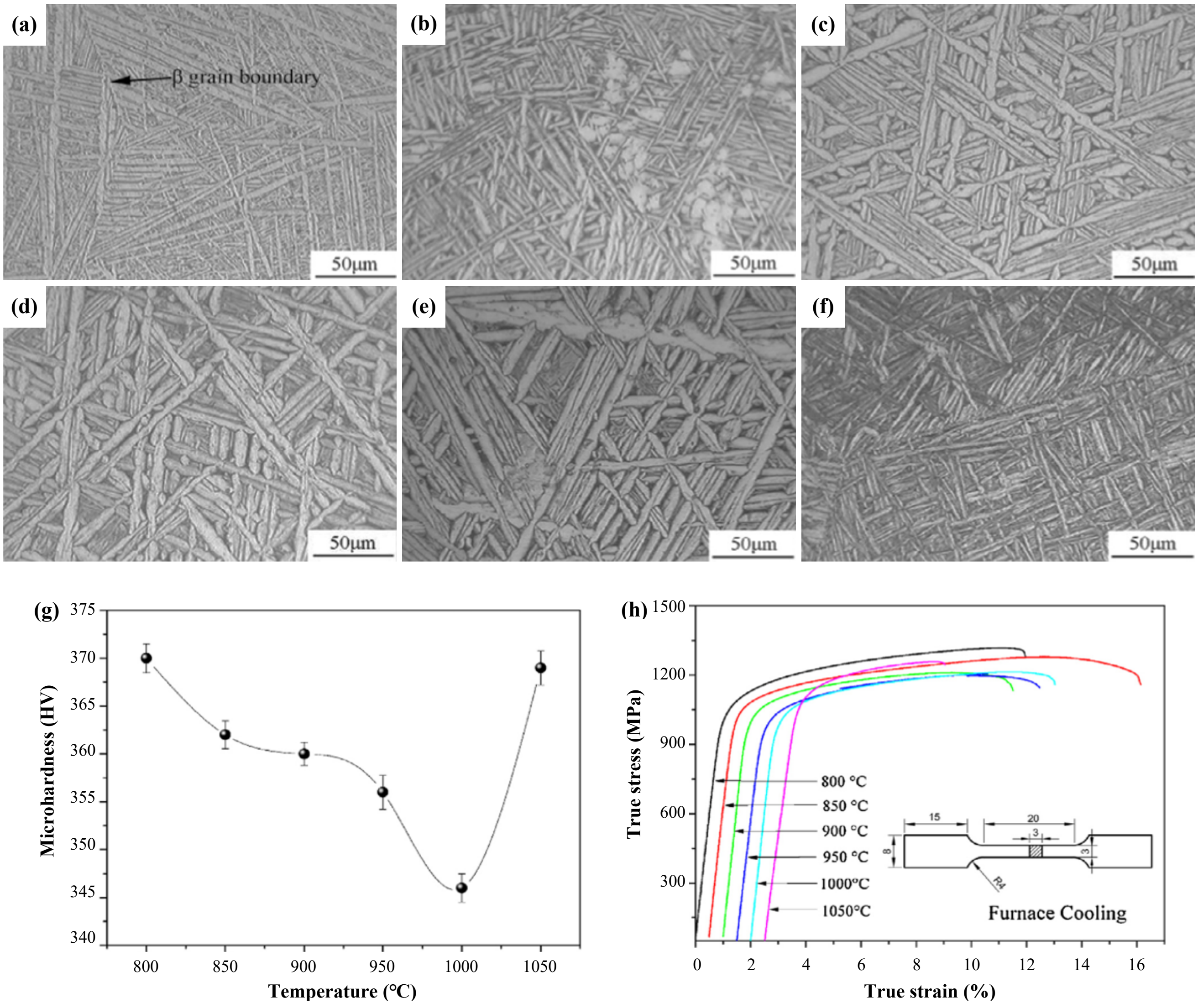

Figure 2. Microstructure and mechanical properties of ZrTiAlV alloy at different annealing temperatures: (a) 800°C; (b) 850°C; (c) 900°C; (d) 950°C; (e) 1000°C; (f) 1050°C; (g) Microhardness; (h) True stress–strain curve 0.

Table 1. Performance parameters of high strength and toughness Zr alloys 0.

Alloys	Phase	Heat treatment process	σ_b (MPa)	ε (%)
Zr1.5Sn6Al	α+β	890°C Hot rolling and quenching	847	15.35
Zr1Be	α+Be_2Zr	850°C Hot rolling and quenching	892	7.06
Zr35Ti	α'	620°C Hot rolling and quenching	1063	7.0
Zr3Cr	α+$ZrCr_2$	870°C Hot rolling and quenching	1270	6.0
Zr45Ti5Al3V	α+β	930°C Hot forging air-cooling +700°C 1h Furnace cooling	1301	9.5
Zr46Ti7Al	α	800°C Hot rolling air-cooling	1564	10.1

3. Toughening mechanism of new high tensile Zr alloys

Currently, the performance of Zr alloys as structural materials for applications still needs to be improved, and it is necessary to improve the mechanical properties of Zr alloys so as to ensure their safety in service. The commonly used methods to improve the mechanical properties include alloying, amorphization and hot working process.

3.1 Alloying

The alloying method is mainly based on the addition of different elements required in the Zr metal matrix, followed by different processes to adjust the microstructure and morphology of the alloy to obtain the final desired alloy properties. Different compositions and specific processes are used to adjust the alloy, which can exhibit multiple enhancement mechanisms. Zr alloys show preferential mechanical properties when they contain Ti, Sn, Nb, Al, Cr, V, B, Be, Ta, and so on. The addition of V elements can improve the mechanical properties of the Zr alloy, but at the same time the corrosion performance will be reduced, and adjusting the microstructure of the alloy can effectively improve its adverse effects.

Wang *et al.* [43] choose Ta as the alloying element to analyze the microstructure and mechanical properties of Zr-Ta alloys with different contents of Ta elements. Figure 3(a-f) shows the microstructure of the Zr-Ta alloys, and all the alloys are biphasic except for Zr-1Ta. It is typical net basket tissue morphology. It can be seen from the phase diagram of Zr-Ta binary alloy that with the increase of Ta content, the β→α phase transition temperature of the alloy decreases. The as-cast Zr-Ta alloy did not have sufficient time to grow the α-phase grains during the cooling process. The lower the transformation temperature, the less complete the growth, showing the phenomenon of alloy grain refinement. Sun 0 found a similar phenomenon in the study of α-phase grain growth in TA15 alloy.

Figure 3(g) shows the relationship between hardness and composition of Zr-Ta alloy, from which Zr-Ta alloys have higher Vickers harnesses than Zr and Ta alone, while the hardness of Zr-Ta alloys increases with the increasing Ta content. When Ta is dissolved into the solvent element Zr, the atomic radius of Zr atoms (1.58 Å) is higher than that of Ta atoms (1.43 Å), which leads to the occurrence of lattice distortion in the alloy, and the resistance to dislocation movement generated by lattice distortion increases, which makes it difficult to carry out the slip and increases the solid solution strength of the alloy. Lattice distortion makes it more difficult for dislocations to move, which makes it more difficult for slippage to occur and increases the strength of the solid solution. At the same time, the α slats in the alloy histomorphology will become smaller with the increase of Ta content, due to the increase of small α slats, the grain boundaries become more, the dislocation slip is blocked, and the external force is dispersed by multiple grains.

Figure 3(h) and Table 2 show the engineering stress-strain curves of the Zr-Ta alloy and the mechanical properties parameters of the alloy, respectively. The yield strength and tensile strength of the as-cast Zr-Ta alloy increased significantly with an increase in the Ta element content, as determined by the stress-strain curves. However, the elongation of the alloy decreases at the same time. Using the hardness data with the engineering stress-strain curves, we can see that the Ta elements have a significant impact on the strength and hardness of the alloys. At the same time, strengthening of the Zr-Ta alloy with solid solution and strengthening of the fine grain together simultaneously improves its mechanical properties and increases its strength and toughness. However, the addition of Ta elements can cause lattice distortion and impede dislocation movement, and the interaction between dislocations increases the nucleation points of cracks when plastic deformation occurs in the alloy, and the fine α′ martensite affects the lamellar spacing, and the effective slip length of the α′ lamellar interface affects the nucleation resistance of cracks, at the grain boundaries of the original β grains and the formation of continuous α lamellar clusters in the grain under the action of external forces, the plastic deformation in the local softening zone of Zr-Ta alloy occurs preferentially at the α-phase position at the grain boundaries, which reduces the deformation coordination of the alloy and thus reduces the plasticity of the alloy 0.

3.2 Amorphization

In addition to alloying to enhance the properties of Zr alloys, amorphization can also be used to enhance the strength and hardness of Zr alloys in industry. The principle of amorphization to enhance the properties is that during the very cold solidification of the alloy, the atoms are not able to crystallize in an ordered arrangement and a long-range disordered structure alloy is obtained, which results in an amorphous Zr alloy with very high strength and excellent corrosion and wear resistance, but the poor plasticity of amorphous alloys 0 and their small size greatly limit the prospects of amorphous alloys for industrial applications.

Recent studies have shown that TiZr-based alloys can be enhanced in strength and ductility in the form of crystalline-amorphous nano-structures. It was reported by Ming *et al.* 0 that a TiZr-based alloy containing equiaxed grains consisting of crystalline and amorphous three-dimensional structures (3d-BCANs) was prepared. In situ tensile and compression tests showed that compared to the amorphous and crystalline phases, the BCANs have higher plasticity and strain hardening ability compared with the amorphous and crystalline phases, which can lead to the TiZr-based alloy with high yield strength (1.80 GPa) and better elongation (7.0%).

Table 2. Mechanical Properties of as cast Zr-Ta alloy 0.

Alloy	**E (Gpa)**	**$\sigma_{0.2}$ (MPa)**	**σ_b (MPa)**	**ε (%)**
Pure Zr	71	460.7	525.7	14.02
Zr1Ta	55	566.6	627.1	12.35
Zr2Ta	60	696.8	755.7	13.64
Zr5Ta	66	948.7	1018.3	4.73
Zr6Ta	67	1047.2	1117.3	4.87

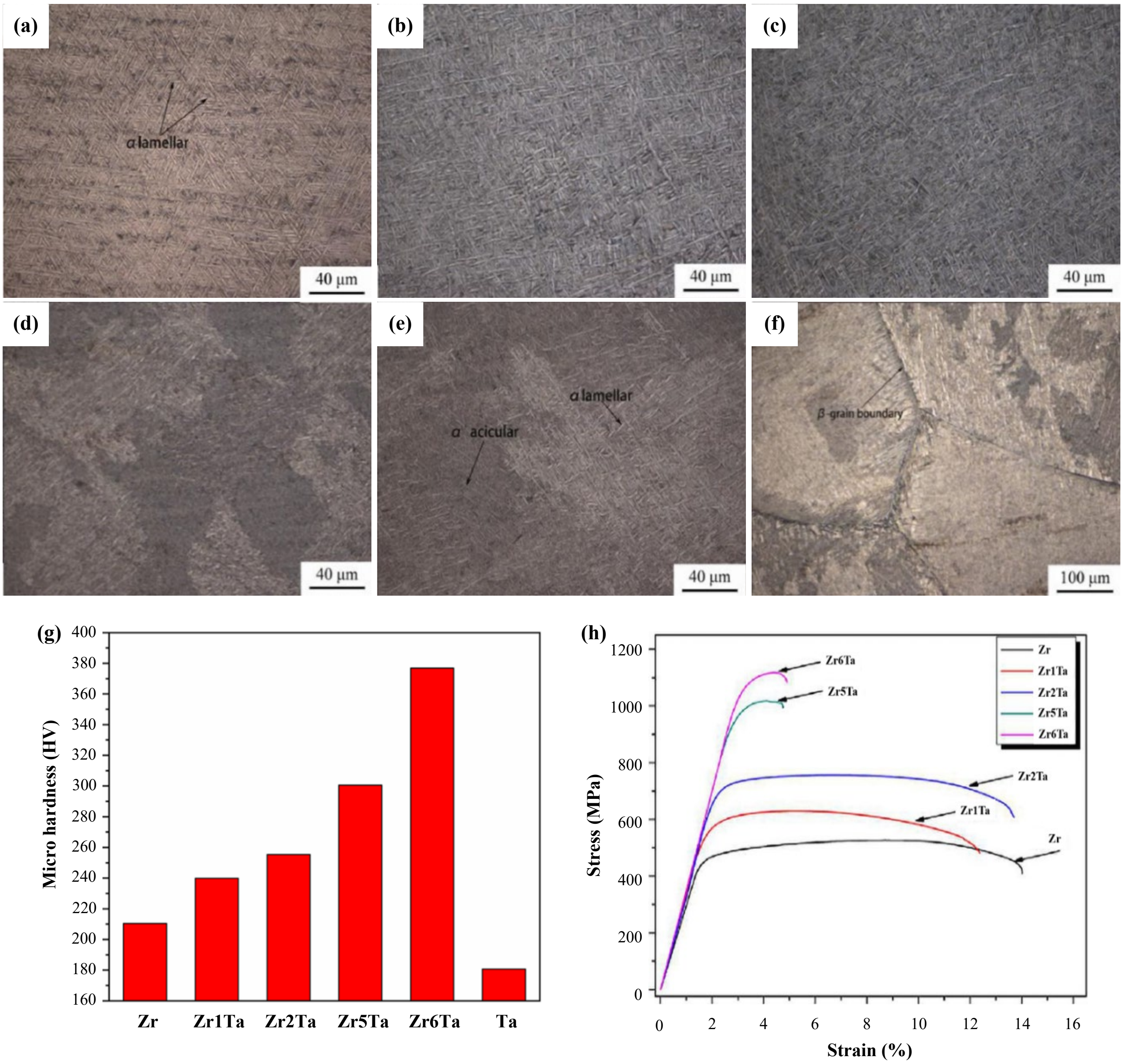

Figure 3. Microstructure and mechanical properties of as cast Zr-xTa alloy: (a) $x = 0$; (b) $x = 1.0$; (c) $x = 2.0$; (d) $x = 5.0$; (e) $x = 6.0$; (f) $x = 6.0$; (g) alloy hardness; (h) stress-strain curve 0.

It is difficult to achieve simultaneous increase in strength hardness and plasticity in general metallic materials. Unlike crystalline materials, the deformability of amorphous materials increases as the characteristic size is reduced to the nanoscale 0. Recent studies have shown that crystalline-amorphous nanolaminates and nanoparticles with amorphous structures can effectively prevent the appearance of shear bands when the amorphous phase size is as small as 100 nm 0. Therefore, it is anticipated that crystal-amorphous composites, consisting of amorphous and crystalline phases of nanometer size, will simultaneously increase both strength and ductility.

Figure 4 presents the compressive stress-strain curve of the 3D-BCAN single crystal column and the topography of the slip and shear bands. Compared with the other two kinds of single crystal column and amorphous column, the yield strength of single-crystal columns of 3D-BCAN is 1.2 GPa with significant strain hardening and no plastic flow instability.

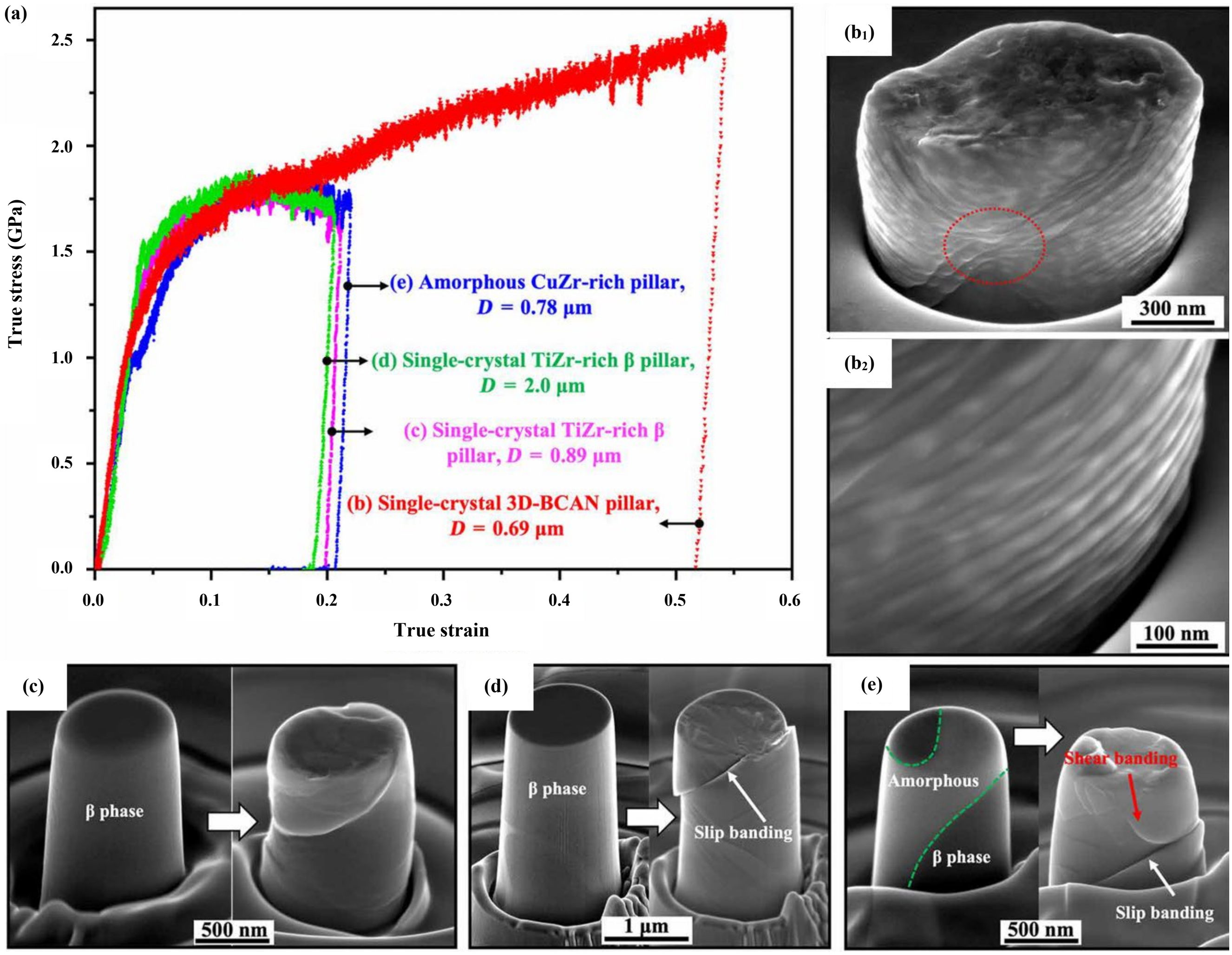

Figure 4. Compressive stress-strain curve of the 3D-BCAN single crystal column and the topography of the slip and shear bands. (a) True stress-strain curves of the single-crystal 3D-BCAN pillars; (b1, b2) Shear band formed by single crystal 3D-BCAN column after compression to 54%; (c-e) Local slip bands (c and d) and shear bands (e) of single-crystal titanium-rich phase columns and amorphous phase columns before and after compression tests 0.

3.3 Thermal processing

Severe plastic deformation (SPD) is an emerging plastic deformation method that introduces large strains during deformation to effectively refine metals to achieve submicron or nanometer scales and obtain complete large-size bulk specimens. By controlling the microstructure during deformation, bulk nanomaterials with high strength and high plasticity characteristics can be obtained. There are many common SPD technologies. This article mainly introduces the Equal Channel Angular Pressing deformation method (ECAP). Zr alloys have a dense hexagonal HCP structure and have less slip systems during plastic deformation. After deformation of Zr alloys by SPD technique, the histomorphology, corrosion and mechanical properties are different compared to conventional deformation 0. ECAP in SPD technique is used to obtain pure shear effect by using corner die, which results in grain refinement.

Cai *et al.* 0 successfully made pure Zr specimens after two passes of ECAP deformation by keeping φ = 105° at room temperature. Compared them with the original specimens, the specimens after ECAP deformation and the specimens annealed at ECAP+350℃. Figure 5 shows the mechanical properties after tensile deformation in these different states. In Figure 5(a-b), the stresses of the ECAP deformed specimens are higher than those of the ECAP+350℃ annealed industrial pure Zr specimens, and much higher than those of the coarse crystals under the same conditions of strain rate and strain. We can find that the tensile strength of industrial pure Zr in different states increases with the increase of strain rate, and the tensile strength of ECAP deformed specimens is greater than that of ECAP+350℃ annealed specimens, and the tensile strength of coarse crystals is lower in Figure 5. In Figure 5(d), the elongation of the coarse crystal is higher than the other two states, which indicates that the plasticity of the coarse crystal is better. Figure 6 demonstrates the tensile fracture morphology of the specimens. It can be seen that the tensile test fracture of coarse crystalline industrial pure Zr has a larger fibrous zone and a larger and deeper tough nest, thus indicating a higher plasticity of the sample. The tensile fracture of the ECAP+350℃ annealed specimens has a smaller niche size between the coarse crystal and the ECAP deformation, so the plasticity is better than the ECAP deformation but worse than the coarse crystal.

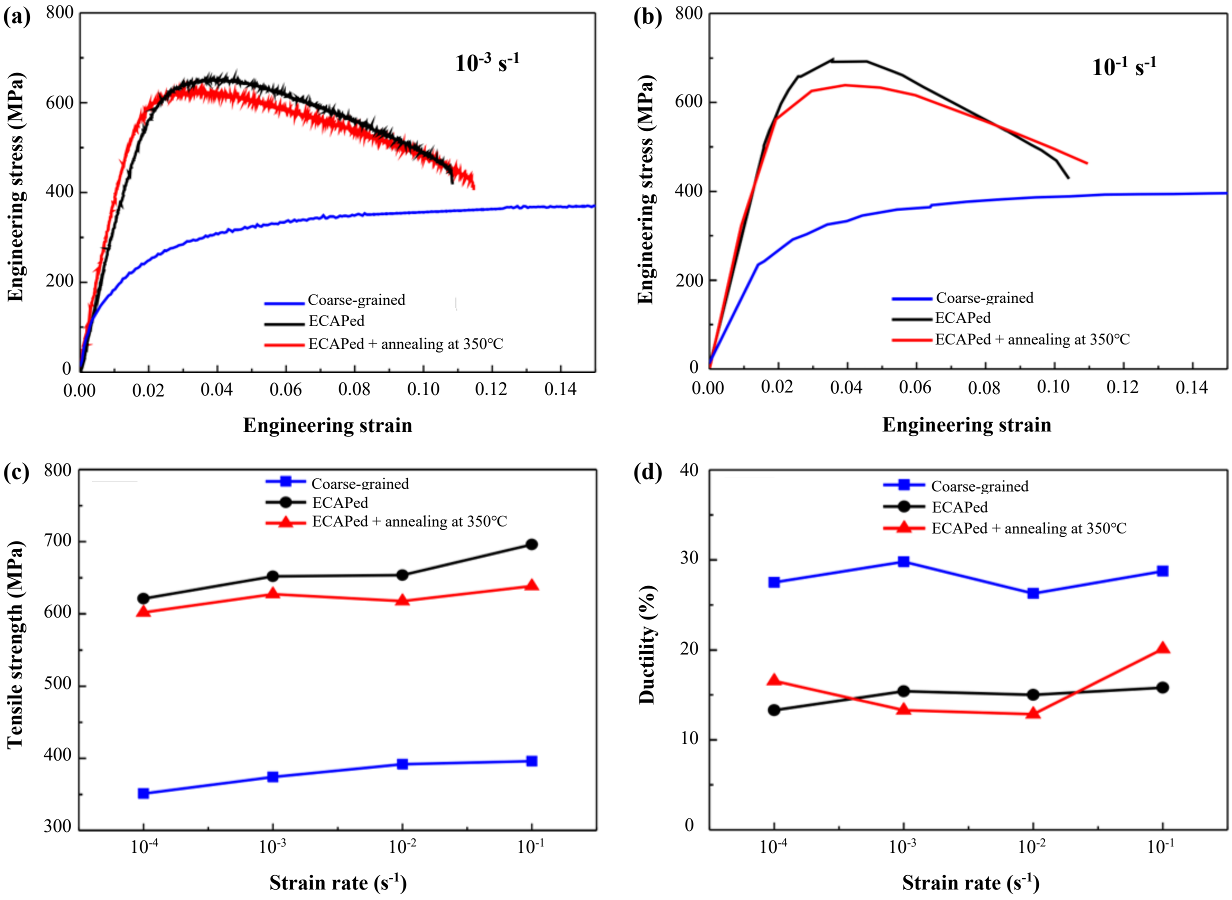

Figure 5. The comparison of mechanical properties of CP-Zr in deferent status: (a) The engineering stress-strain at 10^{-3} s^{-1}. (b) The engineering stress-strain at 10^{-3} s^{-1}, (c) Tensile strength, and (d) Ductility 0.

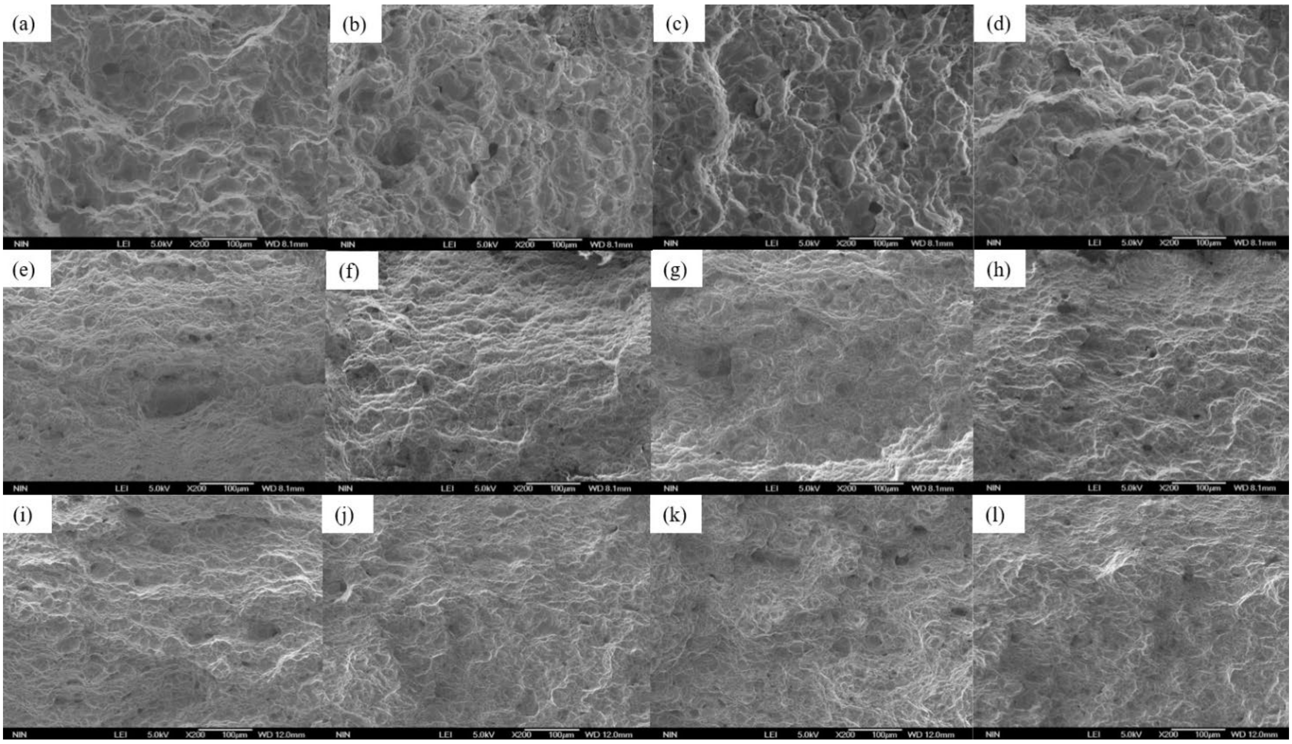

Figure 6. Tensile fractures of industrial pure Zr in different states at strain rates of 10^{-1} s^{-1}; 10^{-2} s^{-1}; 10^{-3} s^{-1}; 10^{-4} s^{-1}: (a-d) coarse crystal, (e-h) ECAP deformation, and (i-l) ECAP + 350°C annealing 0.

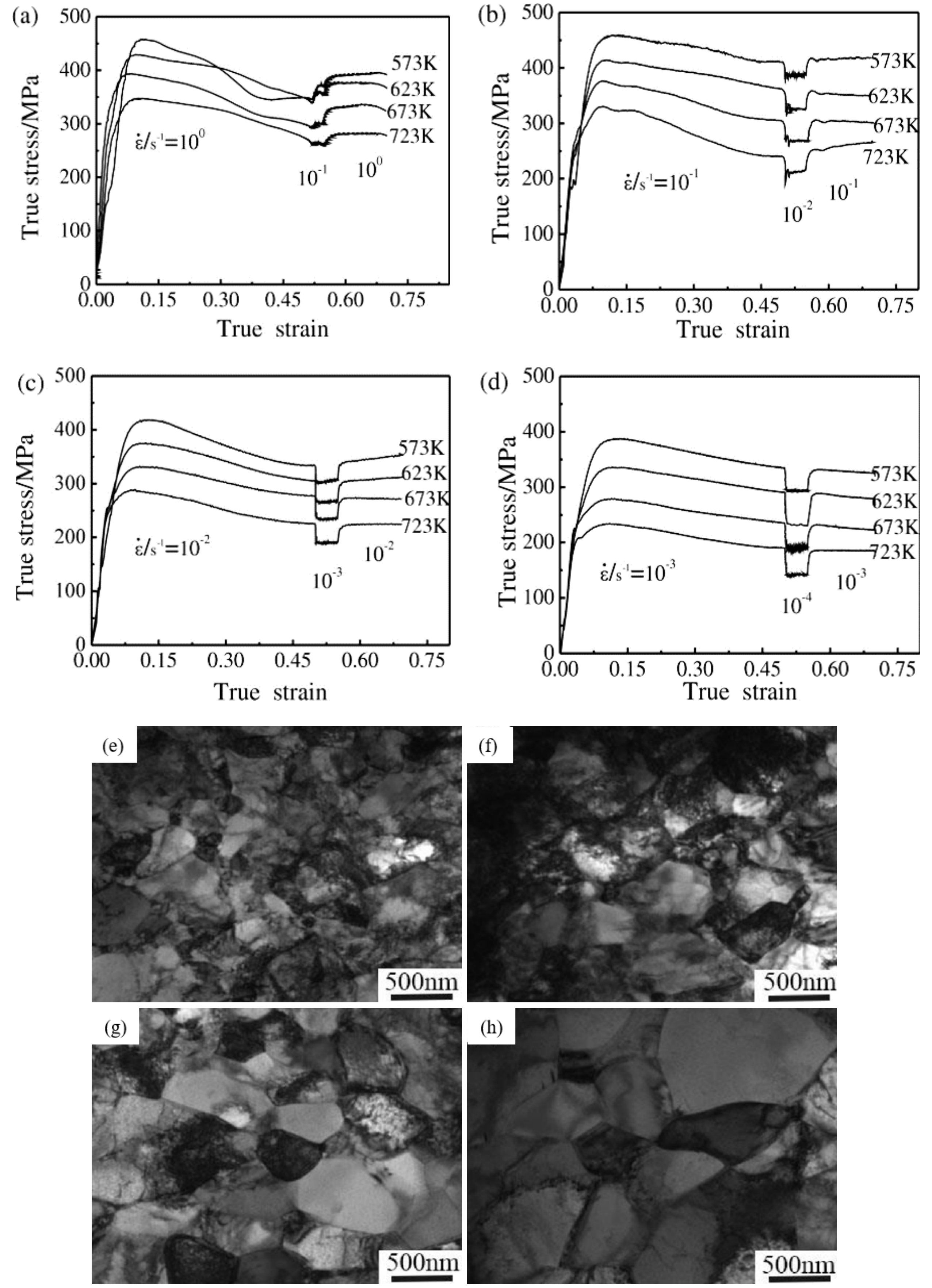

Figure 7. True stress-strain curves and TEM plots of ultrafine crystalline pure zirconium at different strain rates: (a, e) 10^0 s^{-1}, (b, f) 10^{-1} s^{-1}, (c, g) 10^{-2} s^{-1}, and (d, h) 10^{-3} s^{-1} 0

Table 3. Forging and heating process parameters of Zr alloy 0.

Ingot diameter (mm)	Heating temperature (℃)	Holding time (min)
<300	950-980	60-90
300-500	950-980	90-120
>500-800	950-1000	120-300

Yang *et al.* 0 successfully prepared ultrafine crystalline pure zirconium with grain size of about 200 nm to 250 nm at room temperature using ECAP+spin-forging method and performed quasi-static compression experiments on it. Figure 7 shows the stress-strain curves and histomorphology of ultrafine crystalline pure zirconium at different strain rates. It can be seen that the material shows obvious steady-state rheological characteristics. The stress value rises rapidly with the increase of the strain at the early stage of deformation, and then decreases when the stress value reaches the peak, and then gradually enters the steady-state phase. The organization of the material after deformation is mainly dynamic recrystallization organization, and the comparison from Figure 7(e-h) shows that the dislocation density within the organization after deformation gradually decreases and the grains gradually become larger, which is mainly because the lower the strain rate, the slower the deformation and the lower the dislocation density.

Forging is an important part of Zr alloy processing, which is particularly important in the application of Zr alloys. The principle of forging is to reinforced alloys while breaking the original cast structure. In other words, after designing a reasonable billet size, it provides the necessary tissue base for subsequent quenching, extrusion and rolling processes. Table 3 shows the forging heating parameters of Zr alloy 0. It is worth noting that the first final forging temperature of Zr alloy should not be lower than 700℃, and then the temperature can be adjusted appropriately and gradually reduced.

In addition, Zr-based alloys can be reinforced by adjusting appropriate processing parameters (e.g. strain rate, deformation and temperature), additive manufacturing, phase change-induced plastic deformation, twin-induced plastic deformation, etc.

4. Application prospects of new high-strength Zr alloys

4.1 Applications in the nuclear industry

Figure 8 shows the applications if new high-strength Zr alloys. Nuclear energy is a clean energy source with outstanding economic characteristics. In the nuclear industry, the comprehensive performance of nuclear power plant envelope materials will determine the safety and stability of nuclear power plants. To ensure that the efficient and safe operation of nuclear reactors, Zr alloys with high strength and high toughness are usually used as one of the core materials in the nuclear power field. Therefore, Zr alloys are applied in the nuclear industry for wastewater treatment and nuclear power plant construction due to their excellent radiation and corrosion resistance. Besides being used as nuclear fuel casing, Zr alloys are also applied in the production of control rod guide tubes, measuring tubes, heat exchangers and high pressure housings 0. In boil-over solutions of concentrated nitric acid, Zr alloys have been found to have excellent corrosion resistance. Therefore, they can be used as reaction vessel and equipment materials for spent fuel reprocessing 0.

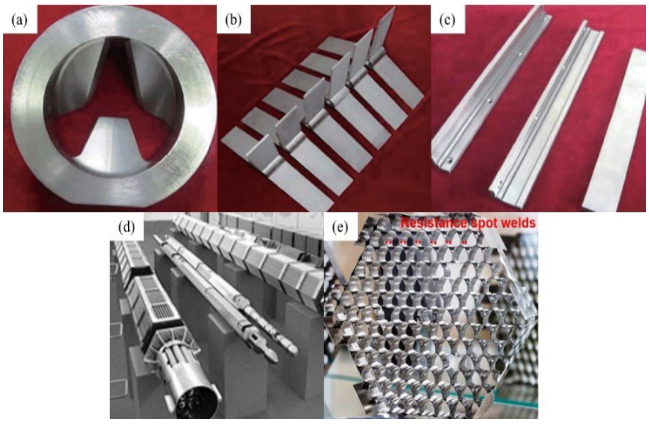

Figure 8. Applications of Zr alloys: (a) Liquid mixer in chemical system, (b) Mixing head in chemical system, (c) Angle slide products of Zr-based alloy, (d) Nuclear Reactor Fuel Assemblies, and (e) Spacer 0.

The Zr alloys currently exploited in nuclear power plants in China are Zirlo alloy, M5 alloy and E110 alloy. However, in order to achieve the goal of Zr alloy localization, China has started to attach great importance to the research and development of nuclear Zr alloys, and has successfully developed NZ2 and NZ8 Zr alloys to meet the requirements of fuel loss control in nuclear power plants. New Fe-Zr alloys are also playing an important role in the development of a new generation of zirconium alloys 0. Since 2020, domestic high tenacity Zr alloys have gained independent intellectual property rights in the nuclear power field and have gradually replaced imported Zr alloy materials, successfully changing the situation of foreign monopoly on the production technology of high tenacity Zr alloy cladding materials.

4.2 Applications in aerospace

Alloys used in aerospace applications should be resistant to radiation irradiation, wear and tear, low temperatures in space, and ultra-high vacuum functions. New Zr alloys have significantly better material properties than conventional alloys so that they are often applied in aerospace. Zr45Ti5Al3V, for example, following core surface treatment, the tensile strength increases from 1400 MPa to 1500 MPa 0. Its excellent mechanical properties can meet the most demanding service environment in the aerospace industry. In addition to the excellent overall performance of the alloy, a series of tests are required to ensure the safety of the material application:

Using charged particles to create irradiation conditions, we tested the surface wear, mechanical properties and nano-hardness of irradiated alloy samples to ensure that high tenacity alloys are safe for service even after being irradiated in a space agency environment.

After atomic oxygen exposure, the resistance to corrosion and wear of the high-strength alloys were significantly improved. After high-speed impact tests on alloy specimens containing 3 km$\cdot$s^{-1} to

9 km·s^{-1} of fine material, the alloys will successively deform plastically and recrystallize, i.e., the deformed alloys can recrystallize and surface harden under high temperature conditions to resist the impact of fine material in the external environment.

At -100°C, alloy samples were tested for tensile strength and elongation. The results revealed the samples had a tensile strength of around 1700 MPa and a 5% to 7% elongation. The tensile strength of the Zr alloy did not change much during the temperature increase from -100°C to 100°C, and thermal expansion coefficient meets the requirement that the air moving parts are in a high precision working condition 0.

4.3 Applications in the chemical industry

Zr and Zr alloys have excellent corrosion resistance and excellent thermal conductivity in most acid and alkali salt solutions and have been comprehensively used in the chemical industry 0. Compared with nuclear Zr alloys, the cost of Zr alloys for chemical applications is greatly reduced because there is no need to consider thermal neutron economy and no separation of Zr and hafnium. In the chemical industry, Zr alloys are generally used in industrial waste gas and wastewater treatment and in the manufacture of methanol recovery units, where they can be used as the main material for reactors, pipes, heat exchangers, etc., to ensure the mechanical properties of each unit.

4.4 Applications in the biomedical field

Due to their excellent corrosion resistance, biocompatibility, and non-magnetic properties, Zr alloys are broadly used in biomedical fields. At present, medical Zr alloys are mainly Zr-Ti-based alloys with controlled non-toxic Ti and Nb element content for biomaterials. Similarly, the addition of Zr to the Ti-Nb alloy system results in hyperelastic recovery strain 0. At present, there are few studies on Zr-Ti-Nb alloys for medical use at home and abroad, and the addition of O elements to them is rare. One of the main reasons is that the existing Zr alloys with high strength and low modulus of elasticity are difficult to be realized simultaneously and do not have obvious advantages in biomedical applications. Secondly, the technology of Zr alloy preparation is limited. When the temperature of Zr exceeds 600°C, it is easily oxidized, and therefore the preparation conditions require a very high vacuum level. In addition, the technical problems of heat treatment of Zr alloys have not yet been solved. However, Zr alloys for biomedical applications have good prospects because Zr itself has a low volumetric magnetization, and the volumetric magnetization of Zr alloys can be further reduced by adjusting the ratio of alloying elements to reduce the effect of magnetic resonance imaging on the surrounding human tissues after implantation, so they are mostly used in the production of vascular stents, dentistry, and other medical devices 0.

5. Summary

According to the current research that in many fields, Zr alloys are commonly used, especially in nuclear technology, aerospace, and chemical production. However, the comprehensive mechanical properties of Zr alloys are not perfect and there is still room for improvement. Researchers should further strengthen the development and preparation of Zr alloys to develop the performance potential of new Zr alloys, so as to further accelerate the industrialization.

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