

Novel ZTE Material with High Seawater Corrosion Resistance

Zr/Ta forms a passive protection layer in air and renders pseudobinary intermetallic (Zr,Ta)(Fe,Co)₂ durable ZTE materials.

Zero thermal expansion (ZTE) materials are deployed in many applications to relieve or avoid thermal stress and are thus essential in engineering applications—for instance, they are used in spacecraft, optical instruments, and containers on liquid natural gas ships. However, most ZTE materials are unstable under harsh conditions, limiting their lifetime and applications in uncontrolled environments. Even commercial invar alloys (Fe–36Ni) rapidly corrode in seawater, moist atmospheres, or phosphate/sulphate solutions. Xianran Xing (University of Science and Technology Beijing, China) and coworkers have researched novel negative thermal expansion and ZTE materials for many years. So far, they have discovered many potential candidates in the binary R_xM_y (using $x:y = 1:2, 1:13, 2:17$, etc.) compound family.^{1–3} Xing, Kun Lin and Xin Chen (both also from University of Science and Technology Beijing, China) reported a new pseudobinary (Zr,Ta)(Fe,Co)₂ alloy (ZTE) in the cubic Laves phase that

exhibits high environmental, cyclic thermal, and phase stabilities.⁴ Thermal expansion and the associated magnetic properties of ZTE were characterized using X-ray powder diffraction, neutron powder diffraction (NPD) at **WOMBAT**, thermodilatometry, and magnetometry. In addition, the chemical stability of ZTE was verified through electrochemical testing, atomic force microscopy, transmission electron microscopy, Auger electron spectroscopy, and X-ray photoelectron spectroscopy.

The coefficient of thermal expansion (CTE), $\Delta l/l_0$, of several $Zr_xTa_{1-x}Fe_{1.7}Co_{0.3}$ compounds is plotted in **Fig. 1(a)** with those of iron and invar for comparison. The thermal expansion of this compound was effectively tuned using chemical modification and optimized to a value of almost zero ($\alpha_1 = 0.21[2] \times 10^{-6} \text{ K}^{-1}$ at $x = 0.2$ [ZTE], 100–360 K). The CTE of ZTE was approximately one order of magnitude smaller than that of invar, despite its slightly

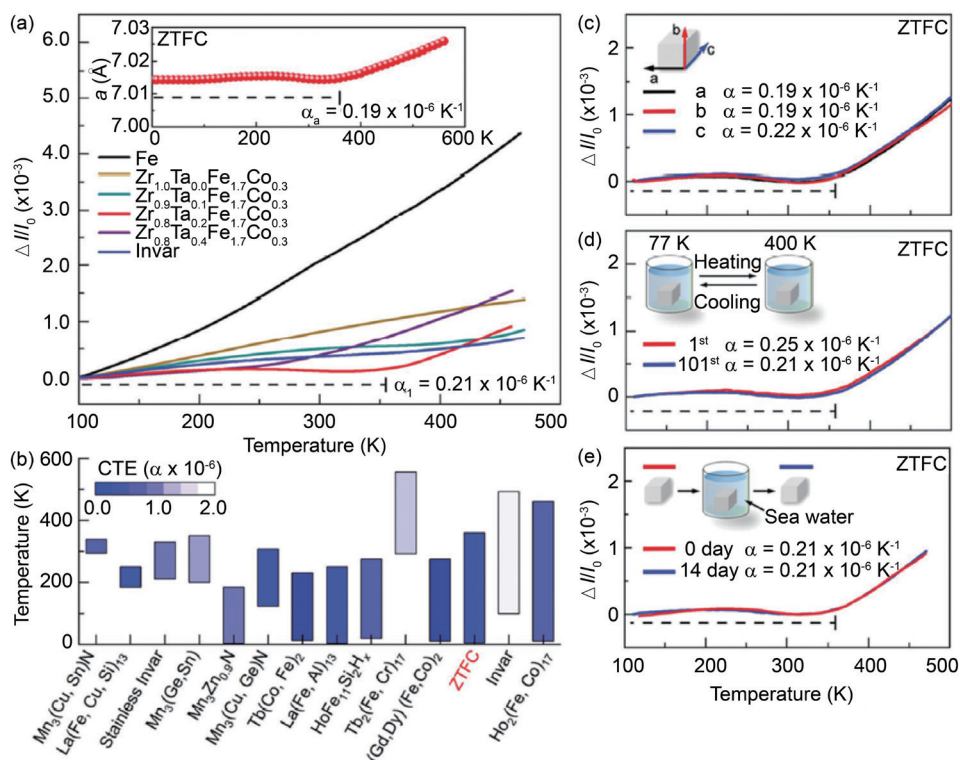


Fig. 1: Thermal expansion of ZTE and related alloys. (a) $\Delta l/l_0$ of $Zr_xTa_{1-x}Fe_{1.7}Co_{0.3}$ ($x = 0-0.4$), Fe, and invar alloys measured using a dilatometer; inset shows the lattice constant a of ZTE measured using neutron diffraction. (b) Comparison of coefficients of thermal expansion and the corresponding temperature windows with conventional ZTE alloys. (c) $\Delta l/l_0$ of ZTE along three perpendicular directions exhibits isotropic thermal expansion. (d) $\Delta l/l_0$ of ZTE in the 1st and the 101st cycles. Each cycle involves a thermal shock from 77 to 400 K. (e) $\Delta l/l_0$ of ZTE before and after immersion in a 3.5 wt% NaCl solution for 14 days. [Reproduced from Ref. 4]

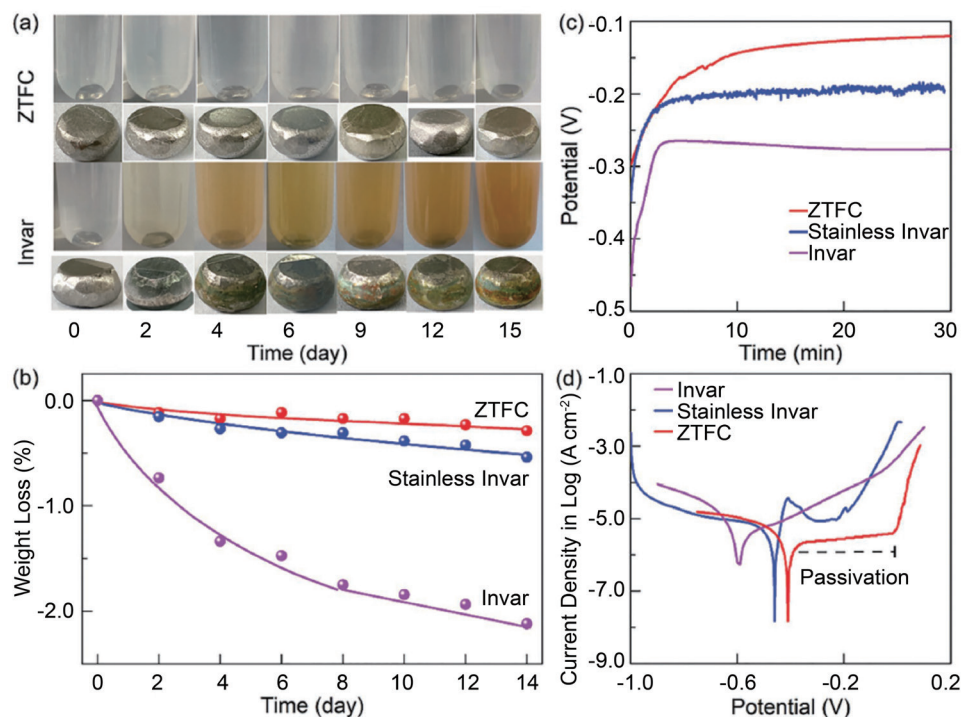


Fig. 2: Environmental stability of ZTFC and related alloys. (a) Photographs of ZTFC and invar alloys immersed in a 3.5 wt% NaCl solution for different durations. (b) Weight loss of ZTFC, stainless invar, and invar alloys during immersion. Electrochemical tests of samples: (c) open-circuit potential (OCP) curve and (d) potentiodynamic polarization (PDP) curve. [Reproduced from Ref. 4]

lower and narrower working temperature range. Many R_xM_y compounds exhibit considerably lower CTE values and slightly lower and narrower working temperature ranges than those of invar, as shown in Fig. 1(b). ZTFC exhibits isotropic thermal expansion characteristics that originate from its cubic crystal structure (Fig. 1(c)). The high durability and stability of ZTFC are indicated by nearly unchanged $\Delta l/l_0$ values after cyclic thermal shock and soaking in 3.5 wt% NaCl solution for 14 days (Figs. 1(d) and 1(e)).

The superior environmental stability of ZTFC compared with that of invar can be immediately identified by soaking ingots in simulated seawater. As shown in Fig. 2(a), ZTFC remained bright with a metallic luster after soaking in NaCl solution for more than 2 weeks, whereas invar became rusty within several days. The rust dissolved in the NaCl solution is reflected in mass loss. ZTFC lost eight times less mass than invar did due to corrosion. Figures 2(c) and 2(d) show the higher environmental stability indicated by a highly noble OCP, -0.12 V, and a slow dissolution rate during the test. The potentiodynamic polarization (PDP) curve of ZTFC exhibits a broader range of gradual incline (voltage ≈ -0.4 to 0 V), which indicates the existence of a stable passive film on the surface of the ZTFC. The existence of this passive film was further confirmed with various experimental tools and was proposed to be the reason for ZTFC's high corrosion resistance. Xing and coworkers suggest that Zr/Ta substitution not only modulates thermal expansion behavior through the indirect modification of Fe/Co magnetic moments but also improves corrosion

resistance by causing the spontaneous formation of passive films of their amorphous oxides. (Reported by Chin-Wei Wang)

This report features the work of Xianran Xing and his collaborators published in Adv. Mater. 34, 2109592 (2022).

ANSTO WOMBAT – High-intensity Powder Diffractometer

- NPD
- Materials Science, Condensed-matter Physics

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