Postprint: Aluminothermic Synthesis of Iron-Based ODS Alloy Co-Strengthened by Nano-Al2O3 and NiAl

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Abstract

Iron-based oxide dispersion strengthened (ODS) alloys co-reinforced with Al2O3 and NiAl were prepared by the aluminothermic synthesis method, and the size, distribution, and movement behavior of Al2O3 nanoparticles were investigated. The results demonstrate that the addition of TiO2 gel facilitates the formation of Al2O3 nanoparticles approximately 10 nm in size. These Al2O3 nanoparticles are entirely bound to NiAl due to interfacial energy effects. When the mass fraction of added TiO2 gel reaches 1.24%, the alloy achieves a maximum tensile strength of 849 MPa while retaining an elongation of 13%.

Full Text

Study on the Thermite Synthesis of Fe-Based ODS Alloys Co-Strengthened by Nanoscale Al O and NiAl

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Abstract

Fe-based oxide dispersion strengthened (ODS) alloys co-reinforced with Al O and NiAl were prepared via thermite synthesis, and the size, distribution, and movement behavior of Al O nanoparticles were investigated. The results demonstrate that adding TiO xerogel can form Al O nanoparticles approximately 10 nm in size, which, driven by interfacial energy, all become associated with NiAl. When the mass fraction of added TiO xerogel reaches 1.24%, the alloy achieves a maximum tensile strength of 849 MPa while maintaining an elongation of 13%.

Keywords: nanoscale Al O , interfacial energy, tensile properties, oxide dispersion strengthened alloy

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Fe-Cr-Al alloys exhibit excellent oxidation resistance and can be used as thermoelectric materials for extended periods above 900 °C. However, their poor high-temperature mechanical properties currently limit their application as high-temperature structural materials. If a thermally stable coherent strengthening phase could be introduced into heat-resistant Fe-Cr-Al alloys, the high-temperature mechanical properties of iron-based alloys could be substantially improved. In the 1970s, Pickering[1] successfully developed 17-7PH ferritic stainless steel strengthened by coherent NiAl precipitates through the addition of Ni and Al alloying elements followed by aging. Subsequent researchers conducted detailed investigations into the growth kinetics of NiAl phase and the mechanical properties of corresponding materials. Taillard and Pineau[2] studied the growth kinetics of NiAl phase in ferrite and the mechanical properties of ferritic alloys, while Zhu et al.[3] investigated the high-temperature creep behavior of FeNiCrAl alloys.

Nevertheless, NiAl-strengthened stainless steels obtained through aging processes have several shortcomings. First, the volume fraction of NiAl phase produced by aging is low, generally below 10%, making the strengthening effect difficult to compare with the ’ phase in high-temperature nickel-based superalloys. Second, the NiAl phase tends to coarsen during high-temperature service, reducing its volume fraction and losing its coherent strengthening effect[3]. Therefore, increasing the volume fraction of the phase and preventing its growth or reducing its growth rate are key to improving the high-temperature mechanical properties of NiAl-strengthened iron-based alloys.

Oxide dispersion strengthening is currently one of the most effective methods for enhancing high-temperature properties. Traditional ODS processes typically employ internal oxidation[4] and mechanical alloying[5-7]. Internal oxidation utilizes alloy elements with low content and strong oxygen affinity to react with oxygen, forming oxide dispersoids as strengthening phases. This method is feasible for certain special metals or simple alloys but problematic for most alloys because it is difficult to prevent other alloying elements from being oxidized. Additionally, the dispersoid size is large and the oxidation degree is difficult to control. Mechanical alloying (MA) is currently the most widely used method, involving high-energy ball milling of atomized pre-alloy powders with fine oxide particles in a protective atmosphere. However, the MA process suffers from uncontrolled oxygen content during high-energy ball milling and is prone to introducing impurities.

Our previous research[8] revealed that using thermite reactions instead of conventional mechanical alloying offers unique advantages in preparing nanoscale oxide-strengthened iron-based alloys. Adding TiO gel to multicomponent thermite mixtures (Fe O +NiO+Cr O +CrO +Al) enables in-situ formation of high-volume-fraction nanoscale Al O particles in the Fe alloy melt. These nanoscale Al O particles often coexist with intermetallic compounds such as NiAl. Furthermore, studies[9-11] demonstrated that designing the composition of multicomponent thermites can generate high-volume-fraction (greater than 50%) NiAl intermetallic compounds in the reaction products. Moreover, the morphology of NiAl phase changes with Al content in the thermite mixture, and at appropriate Al levels, the NiAl phase can appear as an alternating woven morphology with the ferrite matrix. Therefore, thermite reactions can be utilized to in-situ synthesize Al O /FeNiCrAl-NiAl iron-based ODS alloys co-strengthened by NiAl and nanoscale Al O particles with a woven microstructure. More importantly, the in-situ formed nanoscale Al O particles will effectively prevent the growth and coarsening of NiAl phase, maintaining its coherent strengthening effect to higher temperatures and further improving the high-temperature strength and creep resistance of iron-based ODS alloys.

This work employs thermite reactions to in-situ synthesize iron-based ODS alloys with a woven microstructure co-strengthened by NiAl and nanoscale Al O particles, where Al O , NiAl, and the metal matrix are all generated through chemical reactions. By calculating Brownian motion and interfacial energy during nanoparticle movement in the solidification process, we comprehensively analyze how Al O nanoparticles move in the liquid phase and preferentially distribute within the NiAl phase during spinodal decomposition. The relationship between different TiO xerogel additions and the resulting Al O nanoparticles was investigated, along with the mechanical properties of samples, to identify the optimal addition amount for preparing high-performance composites.

Fe-based ODS alloys co-strengthened by Al O and NiAl were prepared using a rapid solidification thermite reaction process. The thermite raw materials mainly consisted of Fe O , NiO, CrO , Cr O , Al powders, and TiO xerogel powders prepared by the sol-gel method with varying contents. The thermite compositions are shown in Table 1 .

The thermite mixture was ground and mixed uniformly before being loaded into a graphite crucible with a hole at the bottom, which was sealed with Al foil. The graphite crucible was placed in an oven and dried at 120 °C for 2 h. After removal, the crucible was positioned on a Cu mold, and the thermite mixture was ignited by electrifying a W filament. A schematic diagram of the experimental setup is shown in Figure 1 [Figure 1: see original paper].

Phase composition analysis of the prepared Fe-based ODS alloys was performed using a D/max-2200PC X-ray diffractometer (XRD) with Cu target, operating at 40 kV and 40 mA with a scanning speed of 6°/min. Microstructure observation was conducted using an OLYMPUS BX51M optical microscope (OM) and a JSM-6010LA scanning electron microscope (SEM). The microstructure of composites was examined using a JEM-2100F transmission electron microscope (TEM) at an accelerating voltage of 200 kV with a resolution of 0.2 nm. TEM samples were prepared by ion thinning using a GL-696F ion mill. Tensile properties were tested using a SANS5100 universal testing machine. Tensile specimens are shown in Figure 2 [Figure 2: see original paper]. Strain gauges (model BX120-2AA, resistance 119.9 Ω, gauge factor 2.08%±1%) were attached to the gauge section of specimens and connected to a JC-4A intelligent static strain recorder to measure elastic strain. The strain gauge curve was fitted with the testing machine curve to obtain accurate stress-strain curves. Three specimens of each type were tested, and the average tensile strength was taken as the final result.

2.1 Microstructure

Figure 3 [Figure 3: see original paper] shows OM images of ODS alloys synthesized with different TiO xerogel contents. Without gel addition, the alloy exhibits equiaxed grains ranging from several tens to 100 µm in diameter (Fig. 3a). With 0.87% TiO xerogel addition, the microstructure remains equiaxed (Fig. 3b), but the grain size decreases to 30–40 µm. With 1.24% TiO xerogel addition, the alloy consists of fine dendrites less than 10 µm in size (Fig. 3c). At 1.98% TiO xerogel addition, the dendrites become larger and more defects appear, including micron-sized black particles (Fig. 3d).

Figure 4 [Figure 4: see original paper] shows the XRD pattern of the ODS alloy prepared with 0.87% TiO xerogel addition. The alloy is mainly composed of bcc ferrite -FeNiCrAl and NiAl phases. The lattice constant of NiAl intermetallic compound is 0.286 nm, extremely close to that of -FeNiCrAl (0.287 nm), so their diffraction peaks largely overlap. However, a weaker superstructure diffraction peak from the NiAl (100) plane appears at 2 = 30.78°, confirming the presence of NiAl intermetallic compound.

Figure 5 [Figure 5: see original paper] shows SEM images of Fe-based ODS alloys. In the sample without gel addition, grains are surrounded by relatively complete gray grain boundary phases (Fig. 5a), and two phases exist within grains: gray and black phases with the black particulate phase being approximately 10 nm in size (Fig. 5b). Combined with XRD analysis, the black phase is identified as NiAl intermetallic compound. With 0.87% TiO xerogel addition, different morphologies appear in intergranular and intragranular regions (Figs. 5c and d). Intergranular regions contain black particulate reinforcement phases, while intragranular regions exhibit a lamellar structure composed of alternating lamellar NiAl reinforcement phase and -FeNiCrAl matrix forming a woven structure. This woven structure is very similar to typical spinodal decomposition microstructures in Fe30Ni20Mn25Al25 alloys, suggesting formation through liquid-phase spinodal decomposition during solidification[12]. With 1.24% TiO xerogel addition, the microstructure changes significantly from equiaxed to fine dendrites (Figs. 5e and f). Particulate phases exist between dendrites, while the intradendritic structure becomes very fine and the woven structure is no longer evident. At 1.98% TiO xerogel addition (Figs. 5g and h), the dendrites become finer and interdendritic regions become smaller and narrower.

Figure 6 [Figure 6: see original paper] shows TEM images and diffraction patterns of the ODS alloy prepared with 0.87% TiO xerogel. As shown in Fig. 6a, -FeNiCrAl and NiAl phases are alternately distributed in a lamellar structure. The narrower phase is continuously distributed in parallel, with lamellae in different directions perpendicular to each other and interconnected. The selected-area electron diffraction (SAED) pattern (area 1 in Fig. 6a) shown in Fig. 6b reveals that the lamellar phase consists of NiAl intermetallic compound and -Al O . The lamellar reinforcement phase is approximately 50 nm wide and 200–500 nm long, with black -Al O uniformly distributed on it at about 10 nm diameter, its formation being related to TiO xerogel addition. Figure 6c shows the SAED pattern of the matrix (area 2 in Fig. 6a), confirming the bcc ferrite -FeNiCrAl structure. The TiO xerogel has a three-dimensional network structure composed of -O-Ti-O- in space, with surface-adsorbed atomic groups such as -OH, -O-COCH , -O-C -O [13,14]. When the reaction temperature reaches approximately 300 °C, these atomic groups leave the gel surface, chemical bonds break, and final carbonization occurs. Simultaneously, the -O-Ti-O- three-dimensional network breaks, O combines with C atoms to form -C-O-Ti-O-C- nanostructures. As temperature continues to increase, C atoms in intermediate oxidation products burn off and volatilize, Al replaces Ti, and finally -O-Al-O- (Al O) nanoparticles form. Nanoscale Al O particles preferentially combine with NiAl phase due to lower interfacial energy[15–20]. Figure 6d shows a bright-field image of the interdendritic region, where blocky particulate phases approximately 50 nm in size exist. The SAED pattern of the blocky phase and surrounding matrix (Fig. 6e) shows the blocky phase remains bcc-structured NiAl and the matrix remains bcc ferrite -FeNiCrAl.

3.2 Formation and Movement Behavior of Al O Nanoparticles

With a melting point of 2045 °C, Al O forms first in the high-temperature melt, and nanoscale Al O particles can only move in the liquid melt. This indirectly proves that NiAl intermetallic compound is not a precipitate phase—Ni and Al element enrichment zones exist in the high-temperature melt, adjacent to Fe and Cr enrichment zones, indicating liquid-phase spinodal decomposition occurred. Since the interfacial energy between nanoscale Al O particles and Ni-Al enriched melt is lower, the combination of nanoscale Al O particles with Ni-Al enriched regions reduces the overall system free energy. TEM analysis (Figs. 5a and b) has proven that Al O nanoparticles are almost entirely distributed on lamellar NiAl phase. The movement of Al O nanoparticles in the high-temperature melt is influenced by both interfacial energy and Brownian motion. Under interfacial energy effects, the particle movement velocity V is given by[21–24]:

$$V = \frac{a_0^3 \Delta\sigma}{6\pi\eta d^n R}$$

where a is the liquid metal atomic spacing,   is viscosity, d is the distance between particle and interface, Δ is interfacial energy, R is particle radius, and n is an exponent. The values are Δ _{Al O } = 1.38 J/m^2[18], Δ _{Fe} = 1.80 J/m^2[19], Δ _{NiAl} = 1.40 J/m^2[20], with a = 0.344 nm,   = 6×10 ^{3} Pa·s[25], R = 5 nm, and n = 4[23]. At 50 nm from the NiAl phase melt, the Al O nanoparticle moving speed V_{Al O -NiAl} = 250 nm/s, while at distances of

5 nm and 10 nm, the speeds are 24.9 µm/s and 3.12 µm/s, respectively. Thus, when influenced only by interfacial energy, Al O nanoparticles move toward NiAl phase, with increasing speed as they approach.

Brownian motion also significantly affects nanoscale Al O particles suspended in the high-temperature melt. When Al O nanoparticles are suspended, they are struck by atoms or atomic groups from different directions. Due to their small size, these impacts cannot cancel out instantaneously, causing continuous changes in velocity and direction and resulting in Brownian motion. According to Langevin theory[26], the average distance S of Brownian motion in any direction for nanoparticles in fluid is:

$$S = \sqrt{2Dt} = \sqrt{\frac{2K_BTt}{3\pi\eta l}}$$

where D is the particle diffusion coefficient, t is time, l is particle diameter, K_B = 1.381×10 ^{23} J/K is the Boltzmann constant, and T is thermodynamic temperature. At 2000 K, the time required for nanoscale Al O particles to move 50 nm under Brownian motion is 2.56×10   s, meaning nanoscale Al O particles can move from Fe-Cr enriched regions to Ni-Al enriched regions within 10   s in the melt. Due to interfacial energy effects, the probability of nanoscale Al O particles combined with Ni-Al enriched regions moving out is much smaller than that of entering. As solidification proceeds, a lamellar structure of nanoscale Al O particles combined with NiAl phase finally forms, exhibiting an overall woven morphology.

3.3 Mechanical Properties of Composites

Figures 7 [Figure 7: see original paper] and 8 [Figure 8: see original paper] show the tensile curves and the variation of tensile strength and elongation with TiO xerogel content in the thermite mixture. Compared with FeNiCrAl-NiAl without nanoscale Al O reinforcement, the tensile and fracture strengths of Fe-based ODS alloys strengthened by Al O nanoparticles are significantly improved. The tensile strengths of alloys prepared with 0.87% and 1.24% TiO xerogel additions are 1.5 and 1.8 times higher than that without gel addition, respectively, reaching 849 MPa with an elongation of 13%. When TiO xerogel addition increases to 1.98%, the tensile strength decreases slightly to 720 MPa, with a corresponding decrease in elongation.

Figure 9 [Figure 9: see original paper] shows tensile fracture morphologies of Fe-based ODS alloys with different TiO xerogel additions. The fracture surface of FeNiCrAl-NiAl composite without gel addition shows typical brittle fracture (Fig. 9a), with clear river patterns and spherical Al O inclusion particles visible on the fracture surface. These large Al O inclusions act as crack sources during tensile loading, which is the main reason for reduced composite strength. After

TiO xerogel addition, Al O nanoparticles gradually increase and fracture morphology transitions to ductile fracture characteristics. With 0.87% TiO xerogel addition (Fig. 9b), the fracture surface contains both equiaxed dimple regions and cleavage fracture regions. With 1.24% TiO xerogel addition (Fig. 9c), the entire fracture surface exhibits uniformly sized dimples without brittle fracture regions. Grain refinement may be the main reason for increased strength and plasticity. Combined with metallographic structures in Figs. 3b and c, when 1.24% TiO xerogel is added, the alloy structure further refines into very fine dendrites. This structural refinement may be related to nanoscale Al O providing numerous nucleation sites for NiAl phase during solidification. Additionally, nanoscale Al O particles dispersed on NiAl phase effectively hinder dislocation movement, also contributing to alloy strengthening. The fracture surface of the sample with 1.98% TiO xerogel addition shows partial ductile fracture (Fig. 9d). Increased gel content in the thermite leads to greater gas evolution during reaction, producing fine shrinkage pores in cast samples that degrade mechanical properties.

Generally, the elongation of most metallic materials decreases with increasing second-phase particle content because conventional second-phase particles are micron-sized. When external loads are applied, stress is transferred to particles through the composite interface, concentrating residual stress on second-phase particles and easily forming voids and cracks[27]. The main reasons for improved mechanical properties with increasing TiO xerogel content in thermite-synthesized Fe-based ODS alloys co-strengthened by Al O and NiAl are: (1) TiO xerogel addition generates Al O nanoparticles that refine the grain structure and improve both strength and toughness; (2) The Al O nanoparticles, approximately 10 nm in diameter and completely combined with NiAl, enhance the strength of NiAl reinforcement phase, thereby improving composite strength.

Conclusions

(1) Fe-based oxide dispersion strengthened (ODS) alloys with a bcc ferrite matrix co-strengthened by NiAl and Al O were prepared through thermite synthesis.

(2) In the high-temperature melt, nanoscale Al O movement is influenced by both Brownian motion and interfacial energy. Since the interfacial energy between Al O nanoparticles and NiAl is lower than that between Al O and -Fe, Al O nanoparticles become associated with NiAl phase.

(3) Adding appropriate amounts of TiO xerogel to the thermite mixture leads to grain refinement and gradual increases in tensile strength and elongation. When TiO xerogel content reaches 1.24%, the tensile strength attains a maximum value of 849 MPa with an elongation of 13%.

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