Optimization of Ball Grading on Microstructure and Mechanical Properties of In-situ Synthesized Al13Fe4/Al Composites via MA-SPS: Post-print

Authors: Hu Na, Xue Lihong, Gu Jian, Heping Li, Yan Youwei

Date: 2023-03-19T00:00:00+00:00

Abstract

Near-fully dense Al13Fe4/Al composites were in-situ synthesized via mechanical alloying-spark plasma sintering (MA-SPS) technique. The microstructure and properties of the materials were optimized by employing grinding ball gradation during the MA process. The microstructure and properties of the powders and sintered specimens were analyzed and characterized using XRD, SEM, TEM, microhardness tester, and mechanical property testing system. The results indicate that under the same MA time, the adoption of grinding ball gradation can effectively improve the ball milling efficiency, leading to a more uniform powder particle size distribution and significantly enhanced solid solubility. After SPS sintering, the microstructure of the composites consists of two phases: α-Al and the intermetallic compound Al13Fe4. The morphology of the intermetallic Al13Fe4 phase is divided into three types: large particles (1–2 mm), ultrafine particles (0.1–1.0 mm), and nanoparticles (20 nm). The large and ultrafine Al13Fe4 particles are formed in-situ through direct reaction between undissolved Fe and Al, whereas the nano-sized Al13Fe4 particles are generated via precipitation of Fe from the supersaturated Al(Fe) solid solution. The Al-10Fe alloy processed with grinding ball gradation contains more large α-Al grains and ultrafine Al13Fe4 particles, thus exhibiting superior comprehensive mechanical properties, with a microhardness of 227 HV, compressive strength of 845.8 MPa, and maximum plastic deformation of 13.6%.

Full Text

Optimization of Grinding Ball Gradation on Microstructure and Mechanical Properties of Al13Fe4/Al Composites In Situ Synthesized by MA-SPS

Hu Na, Xue Lihong, Gu Jian, Li Heping, Yan Youwei

State Key Laboratory of Material Processing and Die & Mold Technology, Huazhong University of Science and Technology, Wuhan 430074

ABSTRACT: Al-Fe alloys are widely applied in automobile, aerospace, military industry and other fields owing to their high specific strength, high specific stiffness, and good microstructural stability originating from the low diffusivity of Fe in Al. However, conventional casting methods lead to inferior mechanical properties of Al-Fe alloys due to coarse microstructures, which cannot meet application requirements. In this work, nearly fully dense Al13Fe4/Al composites were fabricated by combining mechanical alloying and spark plasma sintering (MA-SPS). The effect of grinding ball gradation on the microstructure and properties of the composites was investigated using XRD, SEM, TEM, hardness testing, and compressive tests. The results showed that ball gradation during MA treatment produced more uniform powder sizes and greatly enhanced solid solubility. Furthermore, Al-Fe powders after MA using a single grinding ball size exhibited tiny white Fe particles on the surface of each particle, whereas no such white Fe particles were observed for powders processed with ball gradation. This confirmed that ball gradation was more beneficial for mixing and forming solid solutions of Al and Fe, resulting in more homogeneously distributed powders with smaller average particle sizes of approximately 10 m. After SPS, the composites contained α-Al phase and the intermetallic compound Al13Fe4. Three types of Al13Fe4 were observed: large particles (1–2 m), ultrafine particles (0.1–1.0 m), and nanoparticles (about 20 nm). The large particles and ultrafine Al13Fe4 formed by direct reaction between undissolved Fe particles and Al melt, while the Al13Fe4 nanoparticles originated from precipitation of supersaturated Al(Fe) solid solutions. The sintered sample processed with ball gradation (S2) showed an optimized microstructure with coarser α-Al particles and more ultrafine Al13Fe4 particles, resulting in excellent comprehensive properties: 227 HV microhardness, 845.8 MPa compressive strength, and 13.6% plastic deformation. The combination of abundant coarse α-Al particles and ultrafine Al13Fe4 particles was considered responsible for the high strength and high toughness of the Al-Fe alloy.

KEY WORDS: mechanical alloying, spark plasma sintering, in situ synthesis, Al13Fe4/Al composite, gradation

1 Introduction

As lightweight high-strength structural materials, Al-Fe alloys have attracted extensive attention from materials researchers for their promising applications in automotive, aerospace, and military industries [1–3]. Gilman and Das [4] investigated the Al-Fe alloy system with the intention of using it as a substitute for Ti-6Al-4V to reduce production costs for aerospace components and leverage the advantages of Al-Fe alloys in the aerospace industry. Al-Fe alloys exhibit several notable characteristics: (1) Al and Fe are the two most abundant metallic elements in the Earth' s crust, offering wide availability and low cost; (2) Al has a low density (2.69 g/cm^3) and good ductility, endowing the

alloys with low elastic modulus, high specific strength, and high specific stiffness; (3) the transition metal Fe has a low diffusion coefficient in Al, providing high microstructural stability; and (4) the reinforcing phase is synthesized in situ, ensuring good compatibility with the matrix and strong interfacial bonding [5]. However, Al-Fe alloys prepared by conventional casting methods suffer from coarse microstructures and poor properties, with strength levels far below application requirements. To improve performance, researchers [6–14] have attempted various methods to refine the microstructure of Al-Fe alloys. Huang et al. [6,7], Zou et al. [8], and Krasnowski and Kulik [9] prepared nanocrystalline Al-Fe intermetallic compounds using mechanical alloying (MA). Stolyarov et al. [10] obtained ultrafine-grained structures with grain sizes of 325–450 nm via severe plastic deformation (SPD), achieving a yield strength of 250 MPa and elongation up to 5.8%. Lee et al. [11] fabricated Al-Fe in situ nanocomposites by friction stir processing (FSP) with an elastic modulus of 91 GPa and tensile strength of 217 MPa. Nayaka et al. [12] produced Al-10Fe alloys by rapid solidification processing (RSP) with a microhardness as high as 3.57 GPa. Mukai et al. [13] and Sasaki et al. [14] successfully fabricated bulk nanocrystalline Al-Fe alloys using electron beam-physical vapor deposition (EB-PVD), achieving tensile strengths up to 1000 MPa. While these studies have actively promoted the development and application of ultrafine-grained Al-Fe alloys, their complex processes, difficult control, and low production efficiency have hindered industrial applications.

Mechanical alloying is a common technique for preparing ultrafine powder and non-equilibrium materials [15,16], while spark plasma sintering (SPS) can produce high-density bulk materials with uniform microstructures and fine grains at relatively low temperatures and short sintering times [17–20]. Consequently, the combination of these two processes for fabricating ultrafine-grained/nanocrystalline bulk materials has attracted considerable attention in recent years. Sasaki et al. [2] first employed MA-SPS to produce nanocrystalline Al-5Fe (at%, same below) alloys with compressive strength up to 1 GPa and plastic strain of 30% at room temperature, with the large plastic deformation attributed to deformation of coarse α-Al particles. Our previous work [21,22] also used MA-SPS to prepare Al-10Fe alloys with room-temperature strength as high as 1130.9 MPa, but with almost zero plastic deformation, severely limiting engineering applications. Recently, by adjusting MA process parameters, we optimized the microstructure of Al-10Fe alloys, achieving maximum plastic deformation of 13.6% with slightly reduced strength but significantly improved plasticity and overall mechanical properties. Therefore, this work aims to investigate a key MA process parameter—grinding ball gradation—and its effect on the microstructure and properties of Al13Fe4/Al composites in situ synthesized by MA-SPS, with the goal of obtaining high-strength, high-toughness Al-Fe alloys for potential applications in automotive and aerospace fields.

2 Experimental Methods

The raw materials used were Al powder (99.9 wt%, grain size < 45 m) and Fe powder (99.8 wt%, grain size < 45 m). Al and Fe powders were weighed according to the stoichiometric composition of Al-10Fe and milled in a QM-3SP4 planetary high-energy ball mill for 80 h under vacuum. The ball mill rotation speed was 300 r/min, the ball-to-powder weight ratio was 20:1, and ethanol (4 wt%) was used as a process control agent. The grinding media consisted of stainless steel balls with diameters of 10 mm (large) and 6 mm (small) at a gradation ratio of 1:3. Milling was conducted at room temperature with a 0.5 h cooling break every 5 h. For comparison, Al-10Fe powders were also milled for the same duration using single-size grinding balls (10 mm diameter). For convenience, the original Al-10Fe powder, powder milled with single-size balls, and powder milled with graded balls are designated as P0, P1, and P2, respectively.

The milled powders were loaded into graphite dies with a diameter of 15 mm and sintered in an SPS-3.20MKII spark plasma sintering system under vacuum to produce cylindrical samples 15 mm in diameter and 5 mm in height. The SPS parameters were: heating rate of 60 °C/min, sintering temperature of 550 °C, holding time of 5 min, and applied axial pressure of 80 MPa. The sintered samples prepared from powders milled with single-size balls and graded balls are designated as S1 and S2, respectively.

Phase analysis of the powders and sintered compacts was performed using an XRD-7000S X-ray diffractometer. Grain size and microstrain were estimated using X' Pert HighScore Plus software based on the Scherrer formula [23]. Microstructures of the powders and sintered samples were observed using a Quanta 200 scanning electron microscope (SEM) with an electron backscatter diffraction (EBSD) system. The microstructure of sintered compacts was further investigated using a JEM-2100F transmission electron microscope (TEM), and energy-dispersive spectroscopy (EDS) was employed for elemental analysis. Microhardness of the sintered compacts was measured using an HV-1000 microhardness tester under a load of 2.942 N for 15 s, with the average of ten measurements reported as the hardness value. Compressive mechanical properties were tested using an AG-100KN mechanical testing system on samples with dimensions of 2 mm × 2 mm × 4 mm.

2 Experimental Results

[Figure 1: see original paper] shows EBSD images of Al-10Fe powders before SPS. As seen in Fig. 1a, two types of particles existed prior to milling: white Fe particles and gray Al particles, as confirmed by EDS analysis, distributed independently. After 80 h of milling, no separate Fe particles were observed in either P1 or P2 samples, and the particle sizes decreased. This occurred because repeated plastic deformation, cold welding, and fracturing of Al and Fe powders caused Fe particles to embed and dissolve into Al particles. However, in sample

P1, tiny bright Fe particles were visible on the surface of each particle, whereas this phenomenon was absent in sample P2, indicating that MA treatment with ball gradation was more conducive to mixing and solid solution formation between Al and Fe, resulting in smaller, more uniformly distributed particles with an average size of approximately 10 m.

[Figure 2: see original paper] presents XRD spectra of Al-10Fe powders before SPS. No new diffraction peaks were observed in either P1 or P2 samples after MA treatment, indicating that no Al-Fe intermetallic compounds formed during milling or that the amount formed was too small for XRD detection. Comparison of XRD spectra for P0, P1, and P2 shows that diffraction peak intensity gradually decreased and broadened, while peak positions shifted to higher angles. This demonstrates that Fe atoms dissolved into the Al lattice to form Al(Fe) solid solutions. Since the atomic radius of Fe (0.124 nm) is smaller than that of Al (0.143 nm), Fe dissolution in the Al matrix reduces the Al lattice constant, causing diffraction peaks to shift to higher angles.

Grain size, lattice strain, lattice constant, and Fe solubility in Al were calculated using the Scherrer formula and Vegard's law [24], with the variation curves shown in [Figure 3: see original paper]. The results indicate that powders milled with ball gradation exhibited the smallest grain size (9.75 nm) and lattice constant but the largest lattice strain and solid solubility (6.9 wt%, 3.7 at%). This is because ball gradation enhances milling efficiency, thereby reducing grain size. Additionally, the enhanced milling effect generates numerous dislocations in the Al matrix, which facilitates Fe dissolution in Al and leads to increased solid solubility and lattice strain.

[Figure 4: see original paper] shows XRD spectra of Al-10Fe powders after SPS for samples processed with single-size balls and ball gradation. In addition to α-Al peaks, new phases were identified as the intermetallic compound Al13Fe4.

[Figure 5: see original paper] shows EBSD images of sintered Al-10Fe samples processed with single-size balls and ball gradation. No pores were observed in either sample, indicating near-full-density Al matrix composites. Both samples exhibited similar microstructures consisting of a dark phase A, a white granular phase B, and a gray phase C. Phase B measured 1–2 m and was dispersed in the matrix. Due to the small size of phase C, only phases A and B were analyzed by EDS, with results presented in . The dark phase A contained over 98% Al, identified as α-Al phase, while the white granular phase B contained Al and Fe with an atomic ratio close to 13:4, confirming it as Al13Fe4 phase based on [Figure 4: see original paper]. The morphology of the α-Al phase suggests it formed by melting of powder particle surfaces during sintering. Although the sintering temperature was 550 °C, below the Al-Fe eutectic point of 620 °C [25], the current density at particle surfaces reached extremely high values during initial SPS stages, generating intense Joule heating that raised surface temperatures to the eutectic point, causing melting. Upon cooling, α-Al phase formed along particle surfaces, a phenomenon consistent with mechanisms reported in literature [2,3]. Compared with sample S1 processed with single-size balls, sam-

ple S2 processed with ball gradation contained larger and more numerous dark α-Al phases but fewer white micron-sized Al13Fe4 particles.

3 Analysis and Discussion

[Figure 6: see original paper]a and b show bright-field TEM images of samples S1 and S2 processed with single-size balls and ball gradation, respectively. As seen in [Figure 6: see original paper]a, the C region in S1 consists of short rod-shaped and elliptical ultrafine particles (0.1–1.0 m), black nanoparticles (<100 nm), and a white α-Al matrix. According to literature [21], both the short rod-shaped/elliptical ultrafine particles and black nanoparticles in S1 are Al13Fe4 phase. [Figure 6: see original paper]b reveals that the C region in S2 also comprises α-Al and Al13Fe4 phases, but the Al13Fe4 phase exists as interlaced short rod-shaped ultrafine particles (0.1–1.0 m) and nanoparticles (20 nm). [Figure 6: see original paper]c and d show selected-area electron diffraction (SAED) patterns of the white matrix and short rod-shaped particles, respectively, confirming the white matrix as α-Al phase and the black short rod-shaped particles as Al13Fe4 phase. Moreover, sample S2 contained more ultrafine Al13Fe4 particles than sample S1.

Based on the above analysis, Al13Fe4 phase was dispersed in the α-Al matrix in three morphologies: coarse granular particles (1–2 m), elliptical or short rod-shaped ultrafine particles (0.1–1.0 m), and nanoparticles (~20 nm). The Al13Fe4 nanoparticles formed by precipitation of Fe from supersaturated Al(Fe) solid solutions [2,3], while the other two morphologies likely originated from direct in situ reaction between undissolved Fe and Al during SPS.

Taking Al-10Fe as an example, the amount of Al13Fe4 phase formed by direct in situ reaction was quantified. The volume fraction V of Al13Fe4 phase formed by direct reaction between undissolved Fe and Al can be calculated using the following formula [26]:

Fe × 4 Al × 13 + Fe × 4 Al13Fe4

where MAl and MFe are the relative atomic masses of Al and Fe, respectively, is the density of the sintered compact (3.147 g/cm^3 for Al-10Fe), is the density of Al13Fe4 [27], M is the mass fraction of Fe in the initial powder, and S is the solid solubility of Fe in Al after 80 h of mechanical alloying (mass fraction). The calculated result was 25.1%. Additionally, direct statistical analysis of coarse and ultrafine Al13Fe4 particles using IPWIN Application software yielded a volume fraction of 25.6%, which agrees well with the theoretical calculation (25.1%), confirming that coarse and ultrafine Al13Fe4 particles were formed by direct in situ reaction between Fe that did not dissolve into the Al lattice and Al.

[Figure 7: see original paper] shows compressive stress-strain curves of Al-10Fe samples after SPS. Sample S1 exhibited no yield plateau in its stress-strain curve, indicating negligible or very poor plasticity. In contrast, sample S2 displayed

a distinct yield plateau with plastic strain as high as 13.6%, demonstrating significantly improved plasticity.

Hardness tests were also conducted on the prepared samples, with results shown in . Compared with sample S1, sample S2 exhibited slightly reduced hardness and compressive strength but significantly increased plastic strain.

Material properties depend on microstructure. Statistical calculations and experimental verification revealed that sintered samples S1 and S2 contained the same total amount of Al13Fe4 phase. However, sample S2 had fewer coarse Al13Fe4 particles but more short rod-shaped ultrafine Al13Fe4 particles, along with a greater distribution of coarse α-Al particles ([Figure 5: see original paper]). According to literature [2], coarse α-Al particles are beneficial for improving plasticity. Therefore, the plasticity of the sample was enhanced through the combined effects of coarse α-Al particles and ultrafine Al13Fe4 reinforcing particles.

4 Conclusions

(1) Grinding ball gradation effectively enhances milling efficiency. Al-10Fe powders processed by mechanical alloying with ball gradation achieved a grain size of 9.75 nm and solid solubility of 6.9%, far exceeding the equilibrium solubility limit.

(2) Near-fully dense Al13Fe4/Al composites were obtained by spark plasma sintering. The composites consisted of α-Al and Al13Fe4 phases, with Al13Fe4 present in three morphologies: coarse particles (1–2 m), elliptical or short rod-shaped ultrafine particles (0.1–1.0 m), and nanoparticles (20 nm). Coarse and ultrafine Al13Fe4 particles formed by direct in situ reaction between undissolved Fe and Al, while Al13Fe4 nanoparticles precipitated from supersaturated Al(Fe) solid solutions. Sintered samples processed with ball gradation contained more coarse α-Al particles and ultrafine Al13Fe4 particles.

(3) Sintered samples processed with ball gradation exhibited significantly improved plasticity, with maximum plastic strain reaching 13.6%.

References

[1] Krasnowski M, Kulik T. Intermetallics, 2010; 18: 47
[2] Sasaki T T, Mukai T, Hono K. Scr Mater, 2007; 57: 189
[3] Sasaki T T, Ohkubo T, Hono K. Acta Mater, 2009; 57: 3529
[4] Gilman P S, Das S K. Met Powder Rep, 1989; 44: 616
[5] Koch C C. Mater Sci Eng, 1998; A244: 39
[6] Huang B, Ishihara K N, Shingu P H. Mater Sci Eng, 1997; A231: 72
[7] Huang B, Ishihara K N, Shingu P H. Trans Nonferrous Met Soc, 1999; 9: 747
[8] Zou Y, Sajib S, Kusabirakib K. Mater Res Bull, 2002; 37: 123

[9] Krasnowski M, Kulik T. Mater Chem Phys, 2009; 116: 631
[10] Stolyarov V V, Soshnikova E P, Brodova I G. Phys Met Metall, 2002; 93: 567
[11] Lee I S, Kao P W, Ho N J. Intermetallics, 2008; 16: 1104
[12] Nayaka S S, Murty B S, Pabi S K. Bull Mater Sci, 2008; 31: 449
[13] Mukai T, Suresh S, Kita K. Acta Mater, 2003; 51: 4197
[14] Sasaki, Kita K, Nagahora J. Mater Trans, 2001; 42: 1561
[15] Kim Y W, Griffith W M. Dispersion Strengthened Aluminum Alloys. Warrendale, PA: TMS, 1988: 157
[16] Massalski T B, Okamoto H. Binary Alloy Phase Diagrams. Materials Park, OH: AMS, 1996: 147
[17] Yue M, Zhang J X, Liu X B, Xiao Y F. J Magn Magn Mater, 2004; 2: 271
[18] Xie G, Ohashi, O, Yoshida T, Song M, Mitsuishi K, Yasuda H, Furuya K, Noda T. Mater Trans, 2001; 42: 1846
[19] Olevsky E, Froyen L. Scr Mater, 2006; 55: 1175
[20] Kim C K, Lee H S, Shin S Y, Lewis D B. J Alloys Compd, 2008; 453: 1
[21] Gu J, Gu S S, Xue L H, Wu S S, Yan Y W. Mater Sci Eng, 2012; A558: 684
[22] Gu J, Gu S S, Xue L H, Wu S S, Yan Y W. Acta Metall Sin, 2013; 49: 435 (顾健, 古飒飒, 薛丽红, 吴树森, 严有为. 金属学报, 2013; 49: 435)
[23] Guo J L, Sheng Y N. J Inn Mong Norm Univ, 2009; 38: 357
[24] Pearson W B. A Handbook of Lattice Spacings and Structures of Metals and Alloys. Berlin: Pergamon, 1967: 1
[25] Murray J L. Mater Res Soc Symp Proc, 1983; 19: 249
[26] Yan Y W, Chen Z, Fu Z Y. Acta Mater Compos Sin, 2005; 22(2): 6 (严有为, 陈哲, 傅正义. 复合材料学报, 2005; 22(2): 6)
[27] Villars P, Calvert L D. Pearson' s Handbook of Crystallographic Data for Intermetallic Phases. 2nd Ed., Materials Park, OH: AMS, 1991: 1

Note: Figure translations are in progress. See original paper for figures.