Microstructures and mechanical properties of bulk nanocrystalline Fe–Al–C alloys made by mechanically alloying with subsequent spark plasma sintering

Yoritoshi Minaminoa,*, Yuichiro Koizumia, Nobuhiro Tsujiia, Naoko Hirohataa, Kiyoshi Mizuuchib, Yoshihira Ohkandab

aDepartment of Adaptive Machine Systems, Graduate School of Engineering, Osaka University, 2-1 Yamada-Oka, Suita, Osaka 565-0871, Japan
bMaterials Science and Processing Laboratory, Osaka Municipal Technical Research Institute, 1-6-50, Morinomiya, Joto-ku, Osaka 536-8553, Japan

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Abstract

The microstructure and superior mechanical properties of bulk nanocrystalline Fe–Al–C alloys made by mechanically alloying (MA) with subsequent spark plasma sintering (SPS) were investigated. Three kinds of nanocrystalline Fe–24 at% Al–X at%C (X = 1, 2, 4) alloy powder were produced by MA from iron and aluminum powder with addition of methanol, and were subsequently consolidated at 1073–1273 K under 64 MPa by SPS. These compacts have the relative densities of 99.97% (1 at%C) to 99.5% (4 at%C). The structure of compacts with 1 at%C is composed of grains of Fe3Al of 1.5 μm in diameter and nano κ-carbides (Fe3AlC0.5) precipitates, while those of compacts with 2 and 4 at%C are composed of nanocrystalline Fe3Al of about 80 nm in diameter, nano κ-carbides and small amount of large α-grains of about 1 μm in diameter. These structures maintain the nanostructure even at 973 K, that is, they have the good thermal stability. The mechanical properties of these compacts were measured by compression tests at room temperature (RT) to 973 K in vacuum. The compacts with 1 and 2 at%C of this work perform the superior mechanical properties (e.g. yield strength of 2150 MPa and rupture strain of 0.14 for compact with 2 at%C at R.T.) when compared with the ordinary Fe3Al casting (e.g. the yield strength of 380 MPa and rupture strain of 0.12).

Keywords: Mechanical alloying; Supersaturated solid solution; Fe3Al compound; Fe3AlC0.5 carbide; Spark plasma sintering; Bulk nanocrystalline materials; Compression test; Yield strength; Rupture strain

1. Introduction

Fe3Al intermetallic compound is one of attractive candidates for high temperature structural materials, because it exhibits the superior performances such as high strength, good oxidation resistance and low-cost [1–3]. However, it has some inferior properties to be conquered for commercial applications, such as their poor toughness at room temperature (RT) and limited workability [4]. Generally speaking, there are many means for improvement of the material properties; addition of elements, aging, annealing, quenching, controls of grain boundaries and grain size, and so on. Especially, the combination of addition of elements, grain size refinement and aging will be effective in extensively improving poor properties of Fe3Al compound, because the grain refinement to nanometer size fairly increases the material strength and improves the embrittlement by depressing the propagation of crack, and the addition of carbon element to form fine carbide precipitates strengthens matrix phase and grain boundaries, and suppresses the grain growth.

Bulk metals and alloys with ultra-fine grains are produced by severe plastic deformation processes, such as accumulative roll-bonding [5], equal channel angular pressing [6], and high pressure torsion methods [7]. However, it is very difficult for bulk intermetallic compounds such as Fe3Al to be severely deformed for the grain refinement by above techniques, because most of intermetallic compounds are very brittle. Mechanical alloying technique (MA) can easily produce intermetallic compound powder severely deformed by compression,
friction and shearing due to collision and rub of balls near RT [8]. The MA powders have the various kinds of structures such as the amorphous, nanocrystals and supersaturated solid solutions, because large mechanical energies of severe deformation by MA are introduced to the powder particles, and stored in forms of point defects, dislocations, nanocrystalline interface and so on. In addition, when carbon atoms are included in a process-control agent (PCA) for preventing the powder from adhesion of powder during MA, the carbon atoms are also mechanically alloyed to the MA powder as one of alloy elements.

Basic research and industrial applications of MA powder need the consolidation of powder for the structural materials. Spark plasma sintering (SPS) is a newly developed sintering method, which can rapidly consolidate green compacts to high relative density by applying pressures and passing electric pulse current to the compact [9]. In the beginning of the sintering, the electric pulse current sparks plasma in gaps between the powder particles, and the spark plasma cleans surface by spattering the oxide films and stain on surfaces of powders. The Joule heat due to the electric current rapidly proceeds the sintering of the films and stain on surfaces of powders. The Joule heat due to the electric current rapidly proceeds the sintering of the films and stain on surfaces of powders. This SPS is suitable to consolidate ultra-fine grained powder particles without losing the ultra-fine grained microstructure.

The purpose of this study are to investigate the microstructure and mechanical properties of bulk nanocrystalline (Fe₃Al)₁₋ₓCₓ produced by mechanically alloying the mixture of iron powder and aluminum powder with the methanol as a PCA with subsequent SPS, and to discuss the relation between their microstructures and mechanical properties at RT to 973 K.

### 2. Experiments

Iron powder (20–100 mesh, 99 wt% purity) and aluminum (100 mesh, 99.78 wt% purity) powder were mixed in composition of Fe–28 at%Al. Under an argon atmosphere, 20 g of the mixed powder, 127 g of carbon steel balls of 8 mm in diameter and various amounts of methanol as a PCA were packed in a stainless steel (SUS304) vessel having inner diameter of 50 mm. The amounts of methanol were 0, 0.2 and 1.0 ml.

The MA was carried out with a high-energy planetary ball mill at a centrifugal force of 120G for 7.2–86.4 ks. The inner surface of vessel and the surface of carbon steel balls were coated by first run of MA with the mixed powder of the same initial compositions as each series of operations in order to minimize the infusion of elements from the vessel and balls. The MA powders by second run of MA in series of MA operations were adopted as the samples. Table 1 shows the compositions of the powders before and after MA: the initial compositions of mixed powder taking account of only carbon element in methanol, and the results of chemical compositions measurements. The chemical compositions of aluminum are lower than the initial one, mainly because of the adhesion of aluminum to balls and pot and the mingling of iron from the balls and pot. It is noted that the carbon is included to MA powder without addition of methanol because of the mingling of C from balls and pot.

The MA powder of 20.9 g was consolidated to the discs (milling time; 28.8 ks, and size; 20 mm in diameter and 11 mm in height) with cylindrical graphite and punches at 1073, 1103 and 1273 K under pressure of 64 MPa by using an SPS apparatus whose inner atmosphere in chamber was a vacuum of 2 Pa. The MA powders were heated up at rate of 2 K/s, and then consolidated for 300 s at 1073, 1173 or 1273 K. The cooling rate was about 1 K/s. Hereafter, the MA powders and compacts are referred to as #C-## (=# 1, 2 and 4; carbon contents of 0.86, 1.73 and 4.1 at%C, and ## = MA, 10, 11 and 12; ‘as MA’, consolidated temperatures of 1073, 1173 and 1273 K, respectively). Some of the 1C-12 and 2C-12 were annealed at 973 K for 3.6 ks (respectively referred to as, 1C-12-9 and 2C-12-9).

The microstructures were characterized by optical microscopy, X-ray diffraction method (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The Vickers hardness was measured with a load of 50 gf. The lattice parameters were evaluated from the diffraction patterns of Fe(110), Fe(200), Fe(211) and Fe(220) with those of Si as a standard material. The grain sizes were evaluated from the diffraction angles θ and half-width β of diffraction patterns by Hall’s Eq. (1);

\[
\beta \frac{\cos \theta}{\lambda} = 2\eta \frac{\sin \theta}{\lambda} + \frac{1}{\varepsilon}
\]

where \(\lambda\) is the wave length of X-ray, \(\eta\) the inhomogeneous strain, and \(\varepsilon\) the grain size [10]. The volume fractions of voids in the compacts, \(f\), were evaluated from the optical micrographs on cross sections of the compacts using an image analyzing software (NIH image), and the relative density, \(\rho\), was evaluated as \(\rho = 1 - f\). Disks for TEM observation were cut parallel to the pressure axis from the center of the compacts by an electro-discharge machining, and then mechanically ground to 80 μm thick. The final thinning was done with a dimpling grinder and atom-milling machine. The TEM observation was carried out in the condition of 200 KV, and the corresponding

| Table 1 | Compositions of mixed powders and chemical compositions of MA powders (at%) |
|---------|-------------------------------------------------|
| 1C      | 2C      | 4C      |
| Mixed powder | Fe-28  | Fe-27.6 Al-1.2C | Fe-26.3 Al-5.7C |
| MA powder | Fe-24.7 Al-0.86C | Fe-25.4 Al-1.73C | Fe-24.4 Al-4.1C |
selected area diffraction patterns (SADP) were taken by the use of an aperture of 0.5, 0.8 and 1.6 \( \mu \text{m} \) in diameter. The compression test pieces of \( 2 \times 2 \times 3 \text{ mm}^3 \) in size were cut out of the compacts by the electro-discharge machining. Their surface was polished with 0.05 \( \mu \text{m} \) alumina powder, and the boron nitride powder was applied to the top and bottom surfaces in order to minimize the friction between test piece and compression jigs. The compression direction of test pieces was set up to the same direction of their pressing direction during SPS. The compression tests were carried out at RT to 973 K in vacuum by the Instron-type test machine. The strain rates were \( 1.6 \times 10^{-1} - 1.6 \times 10^{-3} \text{ s}^{-1} \).

3. Results

Fig. 1 shows the X-ray diffraction profiles of the 2C-MA as an example. The as-mixed powder exhibits sharp peaks of pure Al and pure \( \alpha \)-Fe. After MA for more than 14.4 ks, the peaks of Al disappear while the peaks of \( \alpha \)-Fe become broader and their location of diffraction peaks shift to lower angles. This indicates that the \( \alpha \)-Fe solid solution is formed by MA. The broadness of the \( \alpha \)-Fe peaks is maximal at milling time of 28.8 ks. The similar diffraction patterns are also observed for 1C-MA and 4C-MA. Fig. 2 shows the grain sizes and lattice parameters of MA powders evaluated from the X-ray diffraction patterns. The grain sizes decrease with the milling times till 28.8 ks, and thereafter increase slightly. The grain sizes of 1C-MA, 2C-MA and 4C-MA at 28.8 ks are 12, 10 and 8 nm, respectively. On the other hand, all lattice parameters increase with milling times till 28.8 ks, and then become almost constant against MA times. The lattice parameters of the MA powder with higher carbon content are larger; the lattice parameters also increase slightly with the carbon contents. These mean that the Al and C atoms substitutionally and interstitially dissolve into the \( \alpha \)-Fe solid solution respectively, because the atomic radii of Fe, Al and C atoms are 0.124, 0.143 and 0.071 nm, respectively. Thus, the \( \alpha \)-Fe powder of supersaturated solid solutions with crystal grains of about 10 nm was synthesized by the MA for 28.8 ks.

Fig. 3 shows the SEM images of the MA powder milled for 28.8 ks, which were used for consolidation, and the optical micrographs of compacts consolidated at 1273 K for 300 s under 64 MPa by SPS. As shown in Figs. 3(a–c), the powder particle sizes decrease with carbon content; their average sizes of almost equiaxed powder particles are about 27 \( \mu \text{m} \) for 1C-MA, 10 \( \mu \text{m} \) for 2C-MA and 5 \( \mu \text{m} \) for 4C-MA. In Figs. 3(d–f), voids in the compacts are observed as black areas or dots. The \( f \) value of 1C-MA is smallest among the compacts. The \( r \) values of compacts are shown as a function of SPS temperatures in Fig. 4. The \( r \) values increase with increasing SPS holding temperatures and decreasing C contents, and they are more than 99.4%. Especially, the \( r \) value of 1C-12 is a quite high value of 99.97%. Fig. 5 shows the X-ray diffraction profiles of 1C-12, 2C-12 and 4C-12. The X-ray diffraction profiles of compacts consolidated at other temperatures are similar to those at 1273 K. The peaks of Fe$_3$Al and \( \kappa \)-Fe$_3$AlC$_{0.5}$ are apparently observed. These indicate that the supersaturated solid solutions of \( \alpha \)-Fe transform to Fe$_3$Al and the \( \kappa \)-Fe$_3$AlC$_{0.5}$ precipitates during the consolidation by SPS. The amount of \( \kappa \)-Fe$_3$AlC$_{0.5}$ in the compacts increases with carbon content because the intensities of \( \kappa \)-Fe$_3$AlC$_{0.5}$ are stronger in the compacts with much more carbon. Fig. 6 shows the lattice constants and grain sizes of matrix phase in the compacts, along with those of supersaturated solid solutions of \( \alpha \)-Fe phase in the MA powder. As mentioned later, the matrix phase in the 1C compacts is Fe$_3$Al phase, while the matrix phases of the 2C and 4C compacts are composed of Fe$_3$Al phase and small amount of \( \alpha \)-Fe phase. Therefore, the grain sizes and lattice parameters of the 2C and 4C compacts drawn in Fig. 6 represent the values of Fe$_3$Al phase including \( \alpha \)-Fe phase because the X-ray
diffraction patterns of Fe₃Al and α-Fe phases overlap each other. The lattice parameters of the matrix phases of the compacts are comparable to each other against the carbon content and temperatures, and they are lower than that of MA powders. These parameters suggest that the precipitation of κ-Fe₃AlC₀.₅ from the supersaturated solid solution of α-Fe phase low the concentration of aluminum and carbon in matrix phase, resulting in the decrease in lattice parameter of matrix phase. The grain sizes evaluated from X-ray diffraction profiles by Eq. (1) are smaller than those of α-Fe phase.
by TEM observation mentioned later, because the errors in measurement of $b$ values seriously affect the evaluation of grain size, especially for large grain size of more than 50 nm in size. However, these grain sizes are available for evaluation of their relative tendency of grain sizes; the grain sizes of the compacts become larger than that of MA powder due to the grain growth which is enhanced at higher temperatures, and the grain size decreases with increasing carbon content.

Fig. 7 shows the TEM microstructures in the 1C-12, 2C-12 and 4C-12. In the 1C-12, the crystal grains of about 1.5 μm in diameter and very fine precipitates were observed Fig. 7(a). The corresponding SADP indicates that these grains are Fe$_3$Al phases with the $\kappa$-Fe$_3$AlC$_{0.5}$ phases with E2$_1$ structure. This is in accordance with the results of X-ray diffractions as mentioned in Fig. 5. On the other hand, the compacts of 2C-12 and 4C-12 are mainly composed of two regions as shown in Fig. 7(b,c); the aggregations of large grains with average grain size of about 1 μm indicated by the circles of (b1) and (c1), and the aggregations of nano-grains with average grain size of about 80 nm indicated by the circles of (b2) and (c2). In the aggregation of large grains, some of large grains have quite small amount of precipitates inside, and others, which exist around these some grains, have a lot of precipitates. These large grains are the $\alpha$-Fe and fine precipitates are $\kappa$-Fe$_3$AlC$_{0.5}$, as indicated by the SADP from selected area of (b1) and (c1) in Fig. 7(b and c). On the other hand, in the aggregation of nano-grains, the nano-grains of Fe$_3$Al exist with fine precipitates of Fe$_3$AlC$_{0.5}$ as indicated by the SAPD from the selected area of (b2) and (c2) in Fig. 7(b) and (c). As a whole, the aggregations of large grains appear to exist so as to fill in the gaps between the aggregations of nano-grains. The difference in the structures between the 2C-12 and 4C-12 is small, but the region of large grains in 4C-12 is wider than that in 2C-12. However, a few large precipitates indicated by the circle in Fig. 7(d) are observed in 4C-12, and this precipitate is $\kappa$-Fe$_3$AlC$_{0.5}$ as shown in SAPD. Fig. 7 also exhibits the TEM microstructures in the 1C-12-9 and...
2C-12-9, which are 1C-12 and 2C-12 annealed at 973 K for 3.6 ks respectively (Fig. 7(e,f)). The structure of 1C-12-9 is similar to that of 1C-12, but its grain size grows to about 2 \( \mu \text{m} \) that is slightly larger than that of 1C-12. However, the 2C-12-9 exhibits the large grains of 1 \( \mu \text{m} \) in size and nano-grains of 80 nm in size, which are quite similar to those of 2C-12. The structure of 2C-12 is fairly stable and insensitive to the thermal history.

Fig. 8 shows the Vickers hardness of the compacts consolidated at various temperatures by SPS. The values of Vickers hardness increase with carbon content and they are higher than 330 Hv of Fe3Al castings [11]. Especially, the Vickers hardness of 4C-10, 4C-11 and 4C-12 exhibits the higher values than 595 Hv of Fe3AlC_{0.5} [12]. As for the consolidation temperature dependence of Vickers hardness, the experimental values of Vickers hardness for 1C series decreases with increasing consolidation temperatures, but those of 2C and 4C series show a quite small dependence on temperatures. In general, the existence of the voids in the compacts decreases their Vickers hardness. The Vickers hardness of the compacts consolidated at lower temperatures, especially higher carbon compacted at lower temperatures having the lower a lot of voids, is measured to be lower than the inherent Vickers hardness of the compacts without voids. Therefore, the temperature dependence of inherent hardness of the compacts is expected to have a more negative dependence on the temperatures.

Fig. 9 shows the true stress–strain (S–S) curves of the compacts by compression tests at RT in vacuum. The initial strain rate is \( 1.67 \times 10^{-4} \text{ s}^{-1} \), and the arrows indicate the strain over strain of 0.2. The 0.2% proof strengths of all compacts are over 1 GPa, and their rupture strains decrease with carbon content. The 0.2% proof strengths of the 1C-12, 2C-12 and 4C-12 increase with carbon content, while the strengths of 4C-10 and 4C-11 were lowest in the case of the compacts consolidated at the lower temperatures of 1073 and 1173 K. When compared with 380 MPa and 0.12 for the Fe3Al casting, the values of 2C-12 and 1C-12 are more superior; the 0.2% proof strengths of 2C-12 and 1C-12 are 2.15 and 1.09 GPa, and the rupture strains are 0.14 and over 0.2, respectively.

Fig. 10 shows the S–S curves of 1C-12, 2C-12 and 4C-12 by compression tests at elevated temperatures in vacuum. The initial strain rate is \( 1.67 \times 10^{-4} \text{ s}^{-1} \). The shape of S–S curves of 1C-12, 2C-12 and 4C-12 at RT are different each other, but those above 773 K are similar. The S–S curves of 1C-12 at all temperatures show no rupture within strain of 0.2, and the strains of 2C-12 and 4C-12 are more improved at higher temperatures than 673 and 773 K, respectively. The temperature dependence of 0.2% proof strengths of compacts is shown with the result of Fe3Al castings in Fig. 11 [4]. At whole temperatures, the strengths of the compacts are over those of the Fe3Al castings, and the strengths of higher carbon compacts are higher. The 0.2% proof strengths become lower at higher temperatures, and the steep drops in the strengths with increase in temperatures are observed in the compacts with higher carbon...
4. Discussion

The (Fe₃Al)₁₋ₓCₓ (x = 1, 2, 4) compounds made by MA and SPS in this study exhibit the complicated microstructures and small amount of voids relating to the carbon content and consolidation temperatures. Their mechanical properties are more superior to those of ordinary alloys such as the Fe₃Al castings. In order to comprehend these superior mechanical properties, it is prerequisite to elucidate the relations between the structures and mechanical properties by taking account of the morphologies of grain size and precipitates as intrinsic factors and the voids as extrinsic factor.

4.1. Formation of microstructures of compacts

During consolidations by SPS, the structure of super-saturated α-Fe solid solutions with crystal grains of about 10 nm in diameter formed by MA is altered to two kinds of structures as shown in Fig. 7(a) for 1C-12 and Fig. 7(b,c) for 2C-12 and 4C-12. In a very beginning time of SPS, the surfaces of powders suffer a rapid superheating from plasma sparks in gaps and from Joule heat near contact points between powder particles generated by the pulse electric current. The plasma sparks also clean the surface of powder by spattering. This local heating leads to two kinds of alternations in shape and microstructure near the surface of MA powder although the inner part of powder is at low temperatures: in the case (1) where the melting point of powder is high or generation of heat is small, the heated parts near contact points between powders should retain the solid state but become soft enough to be deformed by the applied pressure of 64 MPa, and in the case (2) where the melting point of powder is low or generation of heat is large, some heated parts near the contacts and surface layers of powder should be melt or be in coexistence of solid and liquid. In a moment of softening or melting, the softened solids are deformed or the liquid near the contacts is jammed to the gaps between powder particles by applied pressure of 64 MPa. These deformation and jamming finish the spark of plasma and the generation of the Joule heat by the enlargement of the contact area between powder particles, and immediately the locally heated parts are cooled by the absorption of heat to the inner parts of particles. After those, all parts of powders are subsequently heated up by the heater of carbon dies and consolidated to bulk compacts in the carbon dies under pressures. In the case (1), the compact has the uniform morphology, and in the case (2), it has the complicated microstructures around powders particles.

The 1C-MA corresponds to the case (1), and the 2C-MA and 4C-MA to the case (2), because the melting point of 1C-MA is higher than those of 2C-MA and 4C-MA [13]. The 1C-12 with low carbon content has only the simple structure consisting of Fe₃Al grains of about 1.5 μm in diameter with small amount of very fine κ-Fe₃AlC₀.₅ precipitates (Fig. 7(a)). This morphology easily allows nano-grains to grow from about 10 nm to 1.5 μm because the amount of fine precipitates is not enough to suppress the grain boundary migration by pinning effects. On the other hand, the 2C-12 and 4C-12 have the aggregation area of α-Fe large grains existing between the aggregation areas of Fe₃Al nano-grains with fine precipitates of Fe₃AlC₀.₅ in the inner parts of powder particles (Fig. 7(b,c)). In the very beginning of SPS, the heated parts near the contacts between powder particles by the Joule heat are in the coexistence of the solid having the lower concentrations of carbon and aluminum and the liquid enriched in carbon and aluminum contents. Pressure of 64 MPa preferentially jams the liquid to the gaps, resulting in formation of the areas where the contents are different. These inhomogeneous microconstituent between the regions were reported in the previous paper [14]. As a result, the solid part with the lower concentrations of carbon and aluminum becomes α-Fe large grains having quite small amount of precipitates of κ-Fe₃AlC inside during the subsequent heating up by carbon dies, and the jammed part becomes α-Fe grains having a lot of precipitates of κ-Fe₃AlC₀.₅. This α-Fe phase was formed due to the deficit of Al concentration or the consuming of Al by a lot of precipitation of κ-Fe₃AlC, instead of the Fe₃Al existing in the range of 23–38 at%Al. The amount of the aggregation area of α-Fe large grains in 4C-12 is larger than that in 2C-12. In addition, the 4C-12 has large precipitates of κ-Fe₃AlC₀.₅ as shown in Fig. 7(d). These results also support that the formation process in structure of 2C-12 and 4C-12 is due to the case (2), because the melting point of C4-MA is lower than that of 2C-MA, and the formation of such large precipitates...
of \(k\)-Fe\(_3\)AlC\(_{0.5}\) needs high carbon content and large amount of the liquid layer.

4.2. Relations between mechanical properties and alloy structures of 1C-12

As shown in Fig. 11, the yield strength of 1C-12 is higher than that of the Fe\(_3\)Al castings, and it has the similar temperature dependence to that of the Fe\(_3\)Al castings with grain size of about 50 \(\mu\)m in diameter. The strength of 1C-12 gradually decreases with increasing temperatures similarly to that of castings, and the ductility are over the strain of 0.2. As shown in Fig. 7, the structure of 1C-12 is only the Fe\(_3\)Al grains of about 1.5 \(\mu\)m in diameter with very fine precipitates of the \(k\)-Fe\(_3\)AlC\(_{0.5}\) phases, and the grain slightly grows to about 2 \(\mu\)m in diameter due to the annealing at 973 K. This suggests that the microstructure of 1C-12 slightly changes during the compression test at elevated temperatures up to 973 K. These experimental strengths and microstructures suggest that the deformation mechanism in the 1C-12 with grains of about 1.5–2 \(\mu\)m in diameter is the same mechanism in the ordinary casting; the dislocations more easily move, overcome the pinning by help of activated state and annihilate at elevated temperatures. But, the superior strength and ductility of the 1C-12 to those of the ordinary Fe\(_3\)Al castings are due to the grain refinement to about 1.5 \(\mu\)m in diameter and the pinning effect by a moderate amount of fine \(k\)-Fe\(_3\)AlC\(_{0.5}\) precipitates which suppresses the plastic instability by increasing the work hardening rate.

4.3. Relations between mechanical properties and alloy structures of 2C-12

The yield strengths of 2C-12 are quite high when compared with those of 1C-12, but their ductility is small. The 2C-12 has the aggregation area of \(\alpha\)-Fe large grains of about 1 \(\mu\)m in diameter with small amount of fine precipitates of Fe\(_3\)AlC\(_{0.5}\) and the aggregation areas of Fe\(_3\)Al nano-grains of about 80 nm in diameter with fine precipitates of Fe\(_3\)AlC\(_{0.5}\) in the inner parts of powder particles (Fig. 7(b,c)). In the \(\alpha\)-Fe large grains of about 1 \(\mu\)m in diameter, the deformation is mainly dominated by the dislocation motions as mentioned in the deformation mechanism in 1C-12. Fig. 12 shows the SEM photographs of the surfaces of the 2C-12 compressed at various temperatures. In fact, the large \(\alpha\)-Fe large grains after the compression tests at RT to 773 K have the distinct slip lines, indicating that the deformation in large grains occurs by the dislocation slips (Fig. 12(a–d)).

Fig. 12. SEM images of 2C-12 compressed to 20% plastic strain at (a) RT, (b) 573, (c) 673, (d) 773, (e) 873 and (f) 973 K.
On the other hand, in the nano-grains, it is hard to expect the deformation due to dislocation motions because the number of dislocations in nano-grains is thought to be quite low. Tsuji et al. reported that the nanocrystalline bulk Fe alloys and Al alloys produced by ARB method have poor elongations [15]. Therefore, it is recognized that the mechanical properties of nano-grains such as high strength and low ductility are due to this little motion of dislocations. As shown in Fig. 12(a,b), in the area around the large grains with slip lines, smooth surface was observed at RT and 573 K. This smooth surface indicates that there is almost no deformation in aggregation areas of Fe$_3$Al nano-grains of about 80 nm in diameter with fine precipitates of Fe$_3$AlC$_{0.5}$. In the beginning of the compression the large grains of low strengths are first deformed and then work hardened. The further compression leads to the deformation of nano-grains as well as large grains, but the brittle fracture of nano-grains occurs because nanocrystalline alloys have poor ductility.

The structure of 2C-12 is fairly stable against the thermal history as shown in Fig. 7(b,f). However, the 2C-12 shows the steep drops in the strength around 773 K. At higher temperatures than 673 K, the rugged surface is observed in the area around the large grains and their degree of roughness become larger with increasing temperatures (Fig. 12(c–f)). The unit size of roughness of rugged surface is about 80 nm to 120 nm, which correspond to the grain size of nano-grains in 2C-12 and 2C-12-9. These rugged surfaces suggest that the deformation occurs in the aggregation area of nano-grains and the amounts of the deformations become larger as the temperature of compression test rises. This deformation mode improves the ductility such that the ruptures are not observed within the strain less than 0.2, but it decreases the yield strength at 773 K to about half of that at RT.

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At the higher temperatures of 873 and 973 K, the distinct steps due to slip lines in the large grains are not observed. Fig. 13 shows the TEM microstructures of 2C-12 after severe compression test to reduction of 50% at 973 K, where the compression test was carried out at by $10^2$ times larger strain rate of $1.67 \times 10^{-2} \text{ s}^{-1}$ in order to increase the dislocation density. The crack was not observed even after 50% deformation. In the large grains indicated by the circle of (A), the dislocation cells are observed; there is a small misorientation between the areas divided by the dislocation cell, as indicated by the SADP from the area of (a) whose spots are stretched. This means that the deformation occurs by the dislocation motions with small amount of dynamic recovery.

On the other hand, Fig. 12(e and f) show that the roughness in the aggregation area of nano-grains become more visible and larger and the shape of roughness becomes somewhat elongated in the direction perpendicular to compression axis. As also shown by the circle of (B) in aggregation area of nano-grains of Fig. 13, the nano-grain size is about a few hundred nm, which is greater than that in the compact compressed to 20% of reduction at 973 K. This grain growth is mainly due to the increase in the driving force of grain growth by the high dislocation density caused by the large deformation to 50% strain at high strain rate. Furthermore, the shape of grains is also fairly elongated in the direction perpendicular to the compression axis. These elongated grains are fairly corresponding to the roughness on the surface. This suggests that the deformation in the aggregate area of nano-grains is mainly due to the dislocation motions.

Fig. 14 shows the strain rate dependence of the deformation of 2C-12 by compression test at 773–973 K. There is an empirical relation between the stress $\sigma$, 

![Fig. 13. TEM images of 2C-12 after compression test to a reduction of 50% at a strain rate of $1.6 \times 10^{-2} \text{ s}^{-1}$ at 973 K.](image-url)
strain ε, strain rate ˙ε and temperature T;

\[ \sigma = A e^{k \varepsilon^m \exp \left( \frac{Q}{RT} \right)} \]  

(2)

where A and k are constants, m the strain rate exponent, Q the activation energy and R the gas constant [16]. In general, the m values for the deformation by dislocation slips are in the range of 0.02–0.04 at the temperatures from RT to 0.5T_m and 0.1–0.2 above 0.5T_m while they are 0.5 for superplastic deformation and 0.5 for the grain boundary slips [17]. The experimental values of this study are less than 0.1 at 773–973 K. This value strongly suggests that the deformation of the compacts is mainly due to the dislocation slip motions at 773–973 K. Thus, these observations mean that the amount of deformation in large grains reduces, while that in the nano-grains area becomes larger, that is, the deformation in nano-grains area becomes comparable or easy when compared with that in large grains, and the deformation occurs all over the compact, resulting in the decrease in yield strength to about one third of that at RT.

4.4. Relations between mechanical properties and alloy structures of 4C compacts

The compacts of 1C-12 and 2C-12 have the high relative densities above 99.9% and perform the superior mechanical properties such as the 0.2% proof strengths of 2.15 and 1.09 GPa and the rupture strains of 0.14 and over 0.2 respectively. Their values of Vickers hardness are 528 and 385 Hv, which are quite high when compared with those of the ordinary Fe₃Al castings. The compression tests at RT to 973 K reveals that the deformation in grains of about 1 µm in diameter occurs by the dislocation slips at all the temperatures and that the deformation in nano-grains also occurs by the dislocation slips at high temperatures of 773–973 K.

5. Conclusions

The mechanical alloying powders with nano-crystalline grains of Fe-24.7 at%Al-0.86 at%C (referred to as 1C), Fe-25.4 at%Al-1.73 at%C (2C) and Fe-24.4 at%Al-4.1 at%C (4C) were consolidated at 1073, 1173 and 1273 K by SPS method. The relative densities of the compacts with lower carbon content consolidated at 1273 K are the higher values above 99.5%. The 1C compact has the simple structure of Fe₃Al grains of about 1 µm in diameter with fine precipitates of Fe₃AlC₀.5, while the 2C and 4C compacts have the complicated structures consisting of the aggregate area of α-Fe grains of about 1 µm in diameter and the area of the Fe₃Al nano-grains of 80 nm in diameter, in which fine precipitates are dispersed.

The compacts of 2C and 1C consolidated at 1273 K perform the superior mechanical properties such as the 0.2% proof strengths of 2.15 and 1.09 GPa and the rupture strains of 0.14 and over 0.2 respectively. Their values of Vickers hardness are 528 and 385 Hv, which are quite high when compared with those of the ordinary Fe₃Al castings. The compression tests at RT to 973 K reveals that the deformation in grains of about 1 µm in diameter occurs by the dislocation slips at all the temperatures and that the deformation in nano-grains also occurs by the dislocation slips at high temperatures of 773–973 K.

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