Ultrafine processing of (TiB+TiC)/TC18 composites processed by ECAP *via* Bc route

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Abstract

Equal channel angular pressing provides a convenient approach to introduce ultrafine grain size into commonly used metallic materials. In this study, equal channel angular pressing of (TiB+TiC)/TC18 composite was carried out under different passes *via* route Bc. Microstructure evolution is systematically investigated by optical microscope (OM), scanning electron microscope (SEM), and transmission electron microscope (TEM). The results show that grain boundary sliding contributes much to the plastic deformation and grains are refined largely to 100nm for (TiB+TiC)/TC18 with 0.2% B₄C addition after two passes. The appearance of dislocation accelerates the transformation of spherical α recrystallized grains. Sufficient recrystallization was obtained after three passes. Tensile tests showed that both high strength and elongation appeared in the specimen with 0.2wt% B₄C

addition, which is deformed repeatedly after three passes. Equal channel angular pressing thus be a viable mode for producing titanium matrix composite with both high strength and ductibility.

Keywords: Titanium alloys; Equal channel angular pressing; Microstructures; Mechanical property; Deformation mechanism

1 Introduction

Metallic materials in sub-micron even in nanocrystalline scale were obtained *via* severe plastic deformation through a multi-channel extrusion [1-4]. Recently, some researchers are focusing on the microstructure and mechanical properties of both pure titanium and Ti6Al4V alloys [5-13]. Undoubtedly, equal channel angular pressing (ECAP) is one of the most potential methods of severe plastic deformation (SPD), which can be used to prepare relatively uniform ultrafine-grained metallic materials. Shin *et al.* [6] have investigated the effect of the ECAP on the microstructure and mechanical properties of pure titanium at 350 °C. During the first pass, $\{10\ \bar{1}1\}$ twinning is the main deformation mechanism and dislocation slipping contributed most to plastic deformation after several more passes. Yapici *et al.* [14] reported that much more twins appeared in Ti-6Al-4V during ECAP at 800 °C and only $\{10\ \bar{1}1\}$ twinning was obtained, which also contributed to the major deformation mechanism. In addition, according to former literatures, high strength can also be obtained for pure titanium alloy during ECAP [15-17].

In our previous research, ECAP was employed to refine the grain size of newly developed Ti35Nb3Zr2Ta (wt.%) β type biomedical titanium alloy [18]. The ultrafine equiaxed grains of approximate 300 nm was obtained and the tensile strength can reach to 765 MPa [18]. In present paper, the matrix alloy is TC18 titanium alloy, served especially as high strength and high toughness in aeronautical application [19-20]. Microstructural characteristics and mechanical properties of *in situ* synthesized (TiB + TiC)/TC18 composites have been systematically studied in our former work and the result indicates that the strength, toughness and plasticity of the composite are superior to those of the TC18 alloy [20]. To our knowledge, TiC particles were used to refine the grains of matrix in casting process [21] and impeded the growth of β grains, which is helpful for the formation of the substructures in the deformed phase [22]. In addition, enhancement of the deformed specimen is also attributed to the inclination of the TiB whiskers [23]. Despite the success in processing pure titanium at room temperature by ECAP [9-11], few papers are found mainly on ECAP combined with the enhanced composite technology in titanium alloys. The microstructure evolution and characteristic of reinforcement such as TiC and TiB during ECAP are also not well understood.

In this work, Ti-5Al-5Mo-5V-1Fe-1Cr (TC18) titanium alloy with 0.2 wt% and 0.4 wt% B₄C additions were prepared *via in situ* synthesis method, and then subjected to heat treatment after thermomechanical processing. ECAP was carried out on such specimens and effect of deformation temperature and passes on microstructure

transformation and mechanical properties were investigated. The characteristic of reinforcements during severe plastic deformation was also observed systematically.

2 Experimental procedures

2.1. Raw materials preparation

The raw materials were sponge titanium, B₄C powder (average size was ranged from 5μm to 10μm) and the added Al, Fe, Cr, Al-Mo and Al-V intermediate alloy. The materials were obtained from ingots with the diameter of 120mm by a consumable vacuum arc-remelting furnace. TiB fiber and TiC particles were produced during solidification *via in situ* chemical reactions: $5\text{Ti} + \text{B}_4\text{C} = 4\text{TiB} + \text{TiC}$. The molar ratio of TiB and TiC is designed as 4:1. The temperature of the studied specimen's polymorphic transformation is 890-900°C. The as-cast materials were then forged at 1150°C and followed by rolling at 840°C. Air Cooling was carried out after rolling at 840°C. Table 1 shows the chemical composition of reinforcement particles and metallic matrix of (TiB+TiC)/TC18 titanium matrix composites. #1, #2, and #3 represent the specimens with the B₄C additions at the level of 0, 0.2%, and 0.4%, respectively.

2.2. ECAP processing

ECAP *via* route Bc, continuous rotation of rectangular sample by 90° about the longitudinal axis after each pass, is carried out on YA32-315 four-column universal hydraulic machine. The extruding experiment process is as follows: firstly, adjust the press to a suitable height and preheated mold is placed in a furnace, the samples are also preheated to 100°C as well. Secondly, take out the samples and uniformly coat

with a lubricant, which will be heated to extruding temperature. And then, extrude the specimens at the speed of 80mm/min. After each extrusion, the specimen will be polished and the extruding direction will be changed to 90°. The operating temperature during ECAP was set to 600°C for all of the specimens under one pass, two passes and three passes, respectively.

2.3. Microstructure observations

Microstructure observations were carried out by optical microscope (OM) and field emission scanning electron microscope (SEM). The observed samples were prepared by using conventional techniques of grinding and mechanical polishing followed etching procedure in a hybrid solution (HNO_3 : HF : H_2O =1: 3: 6). The transmission electron microscopy (TEM) observation was conducted using a JEM-2000EX operated at 160 kV. Specimens for TEM were prepared by electrospark cutting to disk with diameter of 3mm and mechanical polishing until the thickness reached below 40 μm . And then a twin-jet polishing is utilized with a solution of 5% perchloric acid, 35% butanol and 60% methanol at a voltage of 20 V and a temperature of -30 °C. All the microstructure observation of the samples oriented parallel to extruded direction during ECAP.

2.4. Tensile tests

Tensile tests were carried out on BTC-T1-FR020TN A50 universal testing machine with maximum load about 20kN at a strain rate of $1.5 \times 10^{-4} \text{ s}^{-1}$ at room temperature. Tensile samples with a nominal gauge length of 20 mm and a

cross-section of $15\text{ mm} \times 1.0\text{ mm}$ were cut by electric discharge machining from the final samples parallel to the extruded direction.

3. Results and Discussions

3.1 Optical microstructure of raw specimens

Figure 1 shows the optical microstructure of as-casted (TiB+TiC)/ TC18 titanium matrix composite with 0.2% B₄C addition. Coarse grain, whisker TiB reinforcement and spherical TiC particles are clearly observed. As indicated in Fig.1(a), trace TiB reinforcement with small length prefers to come out at the grain boundaries, which is consist with the former result in Ref. [24] . Besides the driving force for nucleation of trace reinforcements provided by the grain boundaries with unstable atomic arrangement, solute enrichment of boron (B) and carbon (C) forming in constitutional super cooling, in turn provides the driving force for nucleation and increases the nucleation rate of TiB particles [20]. As shown in the magnified image in figure 1(b), micron TiB whisker around 15 μm in length and TiC spherical particles around 2 μm in diameter are detected along the grain boundary.

3.2 SEM of specimens after first pass

Figure 2 is the SEM microstructure of specimen deformed at 600°C after first pass. The β phase grain size is as small as 10 μm , some of which is even smaller than 1 μm . The reinforcements are precipitating around grain boundaries randomly, which will be considered to play an important role in the sliding of the grain boundaries. It can also be observed that the TiB whiskers are much longer in the

specimen with 0.4% B₄C addition. The lengths of the TiB whiskers range from 10μm to 16μm for the specimen with 0.4% B₄C (figure 2(b)). Comparing with the refined grain, this huger whisker will hinder the further sliding deformation of the specimen and some defects such as pores and cracks will appear due to the inconsistent deformation of the different phases. According to the former researches on the microstructure of the interface of TiB/Ti prepared by *in situ* synthesized technology, there is a flat and sharp interface between TiB whiskers and titanium matrix, with a certain crystallographic orientation relationship [25]. However, during the rectangular extrusion process, large strain accumulation appears. The physical properties of interface on each side between reinforcements and matrix are different. Thus, during ECAP, it is possible that many more defects are obtained on TiB reinforcement. Furthermore, after first pass at 600°C, TiB whiskers debond from the matrix, leaving a few pores with similar size especially in the specimen with 0.2% B₄C addition, as indicated in figure 2(a). According to the previous results [26-27], in the high stress region, due to stress concentration around interface, interfacial shear stress would exceed the yield strength of the interface near the end of short fibers and the yield strength of the interface is reduced gradually as the temperature rises. Thus, interfacial debonding prefers to occur in this area, especially around the TiB particles with low aspect ratios. Meanwhile, the interfacial debonding is also prior for the crack propagation.

3.3 SEM of specimens after different passes

Figure 3 shows the SEM of the (TiB+TiC)/ TC18 titanium matrix composite with 0.2% B₄C addition at 600°C. With the increase of deformation pass, the grain is refined significantly. Nanometer-grain can be obtained under the third pass. Aspect ratio of the TiB decreases with the increase of deformation pass. As reported in former literature, stress concentration increases when the whisker is long, which will accelerate the debonding [28]. Obvious crack propagation caused by interfacial debonding appears, which propagates along certain direction in both specimens ECAPed for both one pass and two passes, respectively, as clearly observed in figure 3(a) and (b). While with the increase of deformation pass, crack propagation seems invisible without significant orientation (Fig.3(c)). In addition, no distinct grain boundaries can be observed and finer grains appears in figure 3(c) herein. Compared with the interfacial debonding happened in the region around the TiB particles with lower aspect ratios, interfacial debonding is also obtained around TiB particles with higher aspect ratios, which is attributed to the accumulative stress concentration *via* this severe plastic deformation after three passes.

3.4 TEM of specimens after different passes

Figure 4 shows the TEM microstructure of (TiB+TiC)/ TC18 titanium matrix composite with 0.2% B₄C addition after first pass, images at different magnification are captured consecutively to show deformation characteristic in details. It can be observed that at low magnification, certain grain orientation appears during ECAP (Fig.4(a)). Grains are refined to nanometer after first pass, seen in figure 4(b). Dislocations assemble together around grain boundary and several dislocation loops

form inside the grain (Fig.4(c)). Meanwhile, the region of dislocations with both high density and low density can be observed. Because of small deformation pass, dislocations with low density appear and obvious dislocation slipping contributes much to the plasticity. Figure 5 shows the TEM of TiB whiskers. During this severe plastic deformation, the orientation of TiB reinforcement is nearly the same to slipping direction, which is caused by the extruding pressing during ECAP. As for the main strengthening particle, the width of the TiB is under 400nm and the length is under 2 μ m, as shown in figure 5(a). Stacking fault is the substructure of TiB whisker, which can be identified in the selected area electron diffraction in figure 5(b). Furthermore, because of *in situ* reaction between the matrix and B₄C, no boundary reaction occurs, which is benefit to the further deformation of the composite.

When the specimen is extruded after second pass, grains are refined largely. Figure 6 shows TEM of (TiB+TiC)/ TC18 titanium matrix composite with 0.2% B₄C addition under second pass. The grain under 100nm is obtained, as shown in figure 6(a). Two grain orientations can be observed, which shows as perpendicular direction. Under second pass, the slipping of grain boundaries turns to vertical direction, which is propitious to the specimen's larger plastic deformation. As shown in figure 6(b) and (c) with higher magnification, spherical α recrystallized grains appears around grain boundaries. Less observed dislocation pileup indicates that the slipping of grain boundaries contributes most to the deformation. Many more dislocations with high density appear because of further ECAP. When the matrix is forced to slip deformation, dislocations piles up at the grain boundaries, when certain level is

reached to produce sufficient grain boundary stress concentration and the dislocation sources in adjacent grains are stimulated, releasing the piled-up dislocation energy. Figure 6(d) shows the microstructure of TiB whiskers. During the second pass, uniformly dispersed TiB with the size below $2\ \mu\text{m}\times\mu\text{m}$ is obtained. No certain deformation orientation can be observed. ECAP significantly improved the uniformity of the particle distribution, similar to the result in Ref.[29]. Continuous shearing in Bc route makes the TiB reinforcements distribute homogeneous. Furthermore, the length of TiB fibers decreases, thus fragmentized TiB particles can be obtained, as clearly indicated in Fig.6(d). The present results are similar to the former results on processing for Al composites [30]. As shown in figure 7, dispersed equiaxed grains appear (Fig.7(a)) and the α recrystallized grains with the diameter around 100nm are obtained (Fig.7(b)). As it is indicated in Fig.7(b), there is orientation relationship between [11-20] zone axis of α phase and [111] zone axis of β phase. During this process, full recrystallization of α phase occurs and dislocation density around grain boundaries decreases largely. Comparing with the specimens deformed after one or two passes, full recrystallization is promoted especially in the third ECAPed specimen, which is also proved in figure 7.

As shown in figure 7(a), totally all equiaxed α grains are obtained in the whole image and the size of each recrystallized grain is under 200nm. During severe plastic deformation, subgrains formed as a result of multilateral processing of the matrix. The dislocation-free region with low energy came out as the valid recrystallized grain core by consuming the dislocations in a high energy region. Therefore, as the increase of

the deformation, many more subgrains appeared which are benefit to recrystallization and grain nucleation. Thus, grains are refined largely when the specimens are deformed through third pass. And obvious high density and low density of dislocations region can be observed in figure 6(c), which is marked as red dash and green dash, respectively. The difference of accumulated dislocation energy from these two regions contributes much to the recrystallization during further deformation.

Accumulative deformation energy contributes much to the dislocation annihilation and recrystallization. Similar phenomenon about recovery of the dislocation structure can also be discussed in Ref. [31]. Figure 7(c) shows the high magnification of spheroidized α recrystallized grains, and several short dislocation lines are observed in the grain likewise. Figure 7(d)-(f) show the morphology of the TiB and TiC reinforcements. TiB whisker with the length around 1 μ m, width around 300nm is obtained and the boundary between TiB and recrystallized grain is clear without other reaction phase, shown in figure 7(e). TiC particle with the diameter of 500nm is observed. Because of low molar content of TiC, a few TiC particles can be observed. While, excellent grain boundary bonding between TiC and matrix is obtained as well, as shown in figure 7(f). Under third pass, homogeneous grains in nanoscale are obtained and uniformly distributed TiB particles contribute much to the homogeneous deformation, which was also proven in the recently published paper focus on the microstructure evolution and mechanical properties of TiB₂/Cu composites processed by ECAP [32]. However, no obvious changes of morphology for TiC can be observed through this severe plastic deformation. While in situ synthesized TiC particles

contribute much to the refined grains of matrix, which is regularly studied in our previous paper [21-22], especially in the following two processes: (1) TiC particle refined the grains during casting and impeded the β grains growth; (2) TiC particle reduced the movement of the grain boundary or dislocation during hot deformation. Clear experimental evidence in present paper can also confirm the previous results. The grain size surrounding TiC particle (marked by the blue circle) is between 150 nm and 200 nm. While the grain size is ranging from 400 nm to 500 nm, which is far away from the particle (marked by the red circle), as shown in Fig.7(f).

3.5 Mechanical properties

Figure 8 shows the stress-strain curve of (TiB+TiC)/ TC18 titanium matrix composite. The yield strength and ultimate tensile strength are both increased during ECAP. Compared with the TC18 alloy, larger value of both yield strength and ultimate tensile strength are obtained in the specimen with 0.2% B₄C addition, which are 1473MPa, and 1509MPa, respectively. As for the elastic modulus, because of the low content of reinforcements, the effect of the B₄C addition on the elastic modulus can also be omitted. However, the refinement of the grain contributes much to the decrease of the elastic modulus. The elastic modulus of the TC18 alloy is 116GPa, while the value is 103 GPa in the 0.4% B₄C added specimen. The lowest value (about 101GPa) is obtained in 0.2% B₄C added specimen. Grain boundaries considered as obstacles play important role to dislocation motion. It is commonly believed that the finer the grain is, the higher the yield strength is. In general, the relationship between yield strength of the material and grain size can be described according to Hall-Patch

equation. Because of smallest grain size, the value of yield strength is the lowest in the specimen with 0.2% B₄C addition. The highest value of ultimate tensile strength is attributed to the smallest grain size as well, which is also confirmed in Refs. [33]. Compared with the strengthening of the reinforcement, fine grain strengthening is much more visible, which can be shown in the specimens with different B₄C additions. Generally, the strengthening effects of particles can be concluded as following two factors: (i) the loadbearing effect of the particles, which is believed that TiB fibers are bearing the tensile stress in the room tensile tests. The contribution of TiB reinforcement was fully proved in Ref. [23]; (ii) the dislocation strengthening in the matrix, which is related to the nucleation of additional dislocations in the matrix [21, 23]. According to the former results about the recrystallized grains accompanying with dislocation annihilation in figure 7, the later factor mentioned above can be decreased especially in the specimen ECAPed for three passes.

The elongation of the alloy is higher than that of composites. Because of the addition of B₄C, stress field appears around whisker TiB and spherical TiC particles. Thus interfacial debonding occurs at the end of dispersed reinforcement. In addition, lots of cavities will immediately generate around the particles, especially for TiB fibers. Therefore, it is difficult for the slipping of the matrix around reinforcements, which decreases the elongation. As for the elongation of those mentioned specimens, larger value is obtained in the specimen with 0.4% B₄C addition under one pass, which contains double value of TiB and TiC. TiB carrying tensile loads can effectively improve the toughness and creep resistance [23,26]. However, the longer

fibers TiB is, the more likely stress concentration will appear, which results in fracture. During this processing, stress concentration is reduced and thus TiB can improve toughness and creep capacity.

As indicated in figure 8 (b), with the increase of extrusion pass, the ultimate tensile strength decreases and the similar values are obtained after both second and third pass, which is around 1450MPa. While largest elongation is observed for the samples processed by ECAP through 3 passes, which reaches to 7.5%. As shown in figure 8(b), large deformation during ECAP is benefit both to equal microstructure and good mechanical properties. Figure 8(c) shows the stress-strain curves of (TiB+TiC)/ TC18 titanium matrix composite with 0.4% B₄C addition under different passes. Ultimate tensile strength and elongation increase after second pass. With the extrusion pass increased, TiB aspect ratio decreases. As mentioned above, TiB can carry tensile load effectively. While the longer TiB is, the more stress concentration appears, which will cause fracture of the specimen. During ECAP, some TiB whiskers break up due to stress concentration. Thus, the average length of TiB is reduced. The shorter TiB fibers can afford more tensile load. Less stress concentration can be observed which will contribute much to improving the ultimate tensile strength and elongation of the specimen. In addition, not the same as TiB, who can effective afford loading, TiC can also prevent the micro-cracks as well as crack propagation.

3.6 Fractograph analysis

Figure 9 displays the SEM of the fracture surface after first pass. The fracture morphologies mainly exhibit toughness fracture in all the specimens, which means

that the specimens tolerate a large amount of elongation before failure appears. As seen in figure 9(a), whirlpool-like pattern is observed. And the whirlpool-like pattern is somewhat different due to the addition of B_4C . The holes are caused by the pulled TiB reinforcements after fracture. As shown in figure 9(b) and (c), when the fiber is perpendicular to the fracture, fiber breakage occurs, which means that the stress concentration is insufficient to make fiber peel. During the tensile processing, crack comes across the fiber to damage, resulting in fracture. This means that the interfacial bonding strength between the reinforcement material and the matrix is high, and the vertical force of the fibers and the matrix is so strong and less prone to debond. The obtained fracture surface pattern thus shows good ductility of (TiB+TiC)/TC18 composites processed by ECAP for both specimens with 0.2% B_4C addition and 0.4% B_4C addition, which also provide an evidence that high fracture strain can be obtained after one ECAP passes.

4 Conclusions

(1) During ECAP, grains boundaries slipping contributes much to the plasticity of the (TiB+TiC)/TC18 composite. The appearance of different dislocations area with high density and low density accelerates the transformation of spherical α recrystallized grains. Sufficient recrystallization can be obtained by three passes.

(2) The reinforcements TiB are rod-like fibers, with the diameter 0.5~2 μm and the length 4~16 μm . The aspect ratio of TiB decreased as press passes increase. This will help to alleviate the stress concentration caused by the large aspect ratio, which

will correspondingly trigger material fracture. Also, there is an excellent interfacial bonding between the in-situ reinforcements and TC18 titanium alloy and the reinforcements of TiB and TiC significantly accelerate recrystallization and thus refine microstructure to nanometer size.

(3) Pressed at 600 °C after first pass, the specimens with 0.2wt% B₄C and 0.4wt% B₄C addition reach 1509 MPa and 1443 MPa, Respectively. While yield strength ($\sigma_{0.2}$) is 1473 MPa and 1403 MPa. Because of sufficient spherical α recrystallized grains appearance, both high strength and elongation are obtained in the specimen with 0.2wt% B₄C addition, which is deformed by three passes. The fracture of the composite matrix belonged to ductile fracture that the microporous generated in the matrix, and gathered around the reinforcements, which were pulled off or pulled out of the matrix.

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Figure Legends

Figure 1 Optical microstructure of as-casted (TiB+TiC)/ TC18 titanium matrix composite with 0.2% B₄C addition: (a) Low magnification (b) High magnification

Figure 2 SEM of ECAP specimens after first pass at 600°C: (a) (TiB+TiC)/ TC18 titanium matrix composite with 0.2% B₄C addition, (b) (TiB+TiC)/ TC18 titanium matrix composite with 0.4% B₄C addition.

Figure 3 SEM of (TiB+TiC)/ TC18 titanium matrix composite with 0.2% B₄C addition under different passes at 600°C: (a) first pass, (b) second pass, (c) third pass

Figure 4 TEM of (TiB+TiC)/ TC18 titanium matrix composite with 0.2% B₄C addition under first pass at 600 °C at different magnification: (a) 5.0K, (b)20.0K,(c)80.0K

Figure 5 TEM of TiB with 0.2% B₄C addition under first pass at 600°C: (a) Low magnification, (b) High magnification and selected area electron diffraction (SAED)

Figure 6 TEM of microstructure of (TiB+TiC)/ TC18 titanium matrix composite with 0.2% B₄C addition under second pass at 600°C at different magnification: (a) 20.0K, (b)66.0K,(c)115.0K, (d) TiB

Figure 7 TEM of microstructure of (TiB+TiC)/ TC18 titanium matrix composite with 0.2% B₄C addition under third pass at 600°C at different magnification: (a) 20.0K, (b)50.0K and selected area electron diffraction (SAED),(c) α recrystallized grains, (d) TiB 6.61K, (e) TiB 50.0K, (f) TiC 15.0K

Figure 8 Stress-strain curve of (TiB+TiC)/ TC18 titanium matrix composite at 600°C: (a) under first pass: #1-1, #2-1, #3-1, represents the specimen with B₄C free, 0.2% B₄C addition, and 0.4% B₄C addition, respectively; (b) specimens with 0.2% B₄C addition under different passes: #2-1, #2-2, #2-3, represents to the specimen deformed with first pass, second pass, and third pass, respectively; (c) specimens with 0.4% B₄C addition under different passes: #3-1, #3-2 is represented to the specimen deformed under first pass, second pass, respectively.

Figure 9 SEM of fractographs of (TiB+TiC)/ TC18 titanium matrix composite under one pass at 600°C: (a) B₄C free, (b) 0.2% B₄C addition, (c) 0.4% B₄C addition

Figure 1a

Figure 1b

Figure 2a

Figure 2b

Figure 3a

Figure 3b

Figure 3c

Figure 4a

Figure 4b

Figure 4c

Figure 5a

Figure 5b

Figure 6a

Figure 6b

Figure 6c

Figure 6d

Figure 7a

Figure 7(b)

Figure 7c

Figure 7d

Figure 7e

Figure 7(f)

Figure 8(a)

Figure 8(b)

Figure 8(c)

Figure 9a

Figure 9b

Figure 9c

Table1 chemical composition of reinforcement particles and metallic matrix (wt.%)

Sample	Al	Mo	V	Fe	Cr	O	Si	B	C	TiB	TiC	Ti
#1	5.5	5	5.2	0.85	0.9	0.08	0.1	0.01	0.02	--	--	Bal.
#2	5.6	5.1	5.2	0.85	0.9	0.08	0.1	0.1	0.06	0.842	0.214	Bal.
#3	5.6	5.1	5.2	0.89	0.89	0.08	0.1	0.2	0.09	1.684	0.428	Bal.