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(19) **United States**(12) **Patent Application Publication** (10) **Pub. No.: US 2007/0209738 A1****Liu et al.**(43) **Pub. Date: Sep. 13, 2007**(54) **HIGH STRENGTH AND HIGH TOUGHNESS  
ALLOY WITH LOW DENSITY AND THE  
METHOD OF MAKING****Publication Classification**(51) **Int. Cl.**  
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(TW)**(52) **U.S. Cl. .... 148/329; 420/72****Correspondence Address:  
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ROSLYN, NY 11576**(57) **ABSTRACT**

The present invention relates to a high strength and high toughness alloy with a low density and the method of making thereof. The alloy essentially comprises 15 to 33 wt % of manganese, 6 to 10 wt % of aluminum, 0.6 to 1.2 wt % of carbon, 0.1 to 1.0 wt % of silicon, and the balance of iron. The alloy has excellent properties of a density of 6.6 to 6.9 g/cm<sup>3</sup>, an elongation of 25 to 70%, and a tensile strength of 100 to 190 ksi. In particular, and the alloy is useful for golf club heads with excellent properties. Further, the use of the alloy reduces pits and defects generated during the electroplating process of the heads. Therefore, the defect rate of the product is remarkably decreased so that the cost is reduced.

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ALLOY NO.	COMPOSITIONS WT%								
	Fe	Mn	Al	Cr	C	Si	Mo	Ti	others
1	Bal.	27.8	8.8	-	0.95	0.28	-	-	
2	Bal.	30.3	8.8	-	1.15	0.16	1.05	-	
3	Bal.	17.5	6.2	-	1.08	0.15	-	-	
4	Bal.	24.9	7.3	-	1.05	0.17	-	-	
5	Bal.	29.1	8.5	-	0.62	0.26	-	-	
6	Bal.	32.1	9.0	-	0.78	0.31	-	-	
7	Bal.	31.6	8.7	-	1.10	0.56	-	-	
8	Bal.	22~36	6~8	-	1.5~2.0	-	1.0~1.5	-	
9	Bal.	26~28	6.5~8	5~6	0.9~1.1	0.2~1.5	1.0~1.2	-	0.9~1.1 Cu 0.02~0.04 Nb
10	Bal.	25~31	6.3~7.8	5.5~9	0.65~0.85	*0.8~1.5	*0.5~1.0	*2~5	
11	Bal.	28~31.5	7.8~10	5~7	0.9~1.1	*0.8~1.5		0.35~2.5	
12	Bal.	25~31	7~10	5~7	0.9~1.1	*0.8~1.5	*0.5~1.0	-	
13	Bal.	23~30	6.3~10	5~9	0.8~1.05	*0.6~1.0	-	-	0.2~10 Co *0.2~0.4 N

\*means content of element optionally added in this alloy.

ALLOY NO.	COMPOSITIONS WT%										
	Fe	Mn	Al	Cr	C	Si	Mo	Ti	others		
1	Bal.	27.8	8.8	-	0.95	0.28	-	-			
2	Bal.	30.3	8.8	-	1.15	0.16	1.05	-			
3	Bal.	17.5	6.2	-	1.08	0.15	-	-			
4	Bal.	24.9	7.3	-	1.05	0.17	-	-			
5	Bal.	29.1	8.5	-	0.62	0.26	-	-			
6	Bal.	32.1	9.0	-	0.78	0.31	-	-			
7	Bal.	31.6	8.7	-	1.10	0.56	-	-			
8	Bal.	22~36	6~8	-	1.5~2.0	-	1.0~1.5	-			
9	Bal.	26~28	6.5~8	5~6	0.9~1.1	0.2~1.5	1.0~1.2	-	0.9~1.1 Cu 0.02~0.04 Nb		
10	Bal.	25~31	6.3~7.8	5.5~9	0.65~0.85	*0.8~1.5	*0.5~1.0	*2~5			
11	Bal.	28~31.5	7.8~10	5~7	0.9~1.1	*0.8~1.5		0.35~2.5			
12	Bal.	25~31	7~10	5~7	0.9~1.1	*0.8~1.5	*0.5~1.0	-			
13	Bal.	23~30	6.3~10	5~9	0.8~1.05	*0.6~1.0	-	-	0.2~10 Co *0.2~0.4 N		

\*means content of element optionally added in this alloy.

Fig. 1

## HIGH STRENGTH AND HIGH TOUGHNESS ALLOY WITH LOW DENSITY AND THE METHOD OF MAKING

### FIELD OF THE INVENTION

**[0001]** The present invention relates to a high strength and high toughness alloy with a low density and the method of making thereof. Due to its characteristics of low density, excellent elongation, high strength and high damping capacity, the alloy is particularly useful for manufacturing golf club heads with large volume, high strength and high toughness to achieve better performance of playing golf. Furthermore, the use of the alloy can efficiently prevent the pits and defects generated during the electroplating process of the heads. Accordingly, the defect rate of the product can be significantly lowered so that the cost is remarkably reduced.

### DESCRIPTION OF THE RELATED PRIOR ART

**[0002]** The characteristics of alloy, such as density, melting point, strength, ductility, thermal conductivity, resistances to corrosion and oxidation, etc., are varied depending on alloying elements. With different requirements for various applications and designs of various mechanical equipments, alloys are made by proper selection of alloying elements and control of the contents, manufacturing procedures and working processes.

**[0003]** For example, Fe—Al—Mn alloys are an alloy series based on the ternary elements. From the extensive studies conducted by the experts in this field, Fe—Al—Mn alloys of low density, high strength, high toughness, high impact energy at low temperature and high oxidation resistance at high temperature or high wearing resistance are obtained by changing their compositions.

**[0004]** A hot-rolled Fe—Mn—Al alloy plate was developed by the present inventors in 1989 with new alloy design concept and has been disclosed in the U.S. Pat. No. 4,968,357, TW Patent 42454, Japanese Patent 1971688, Korea Patent 53613, France Patent 8902580, GB Patent 2227495, Canada Patent 1333556 and Germany Patent 3903774. By properly adjusting the contents of Mn, Al, C elements and adding small amounts of Ti, Nb or V elements, without any subsequent heat treatment, the as-rolled Fe—Mn—Al alloy plate has excellent mechanical properties of a tensile strength of 120 to 200 ksi, a yield strength of 80 to 160 ksi. Meanwhile, elongation and impact toughness are 60 to 30% and 180-40 ft-lb, respectively, which are comparable or even superior to AIS304 and 306 stainless steel, and austenitized, quenched and tempered 9% Ni-steel alloy. By contrast, most commercial alloys have to be heat treated through austenitizing, quenching and tempering processes to reach high strength. For the articles or plates with large size or precision dimension, deformation can be occurred with ease during quenching from the high temperature of austenitizing.

**[0005]** From the extensive studies conducted by the experts in this field, it is found that the corrosion resistance of the Fe—Al—Mn—C alloy is enhanced by adding Cr and Mo alloying elements, as described in the following documents which are incorporated herein by reference:

**[0006]** 1. Jeng-Gong Duh et al., "Diffusion-Related Kinetics in the Oxidation-Induced Phase Transformation of Fe-9Al-3Cr-31Mn Alloys," J. Electrochem. Soc., Vol. 136, No. 3, March 1989.

**[0007]** 2. Jeng-Gong Duh et al., "Micro structural development in the oxidation-induced phase transformation of Fe—Al—Cr—Mn—C alloys," JOURNAL OF MATERIALS SCIENCE, No. 23, 1989.

**[0008]** 3. Jeng-Gong Duh et al., "Nitriding behavior in Fe—Al—Mn—Cr—C alloys at 1000-1100° C.," JOURNAL OF MATERIALS SCIENCE, No. 28, 1993.

**[0009]** 4. S. C. Chang et al., "Environment-Assisted Cracking of Fe-32% Mn-9% Al Alloys in 3.5% Sodium Chloride Solution," CORROSION, No. 51, 1995.

**[0010]** 5. Jeng-Gong Duh et al., "Nitriding Kinetics of Fe—Al—Mn—Cr—C alloys at 1000° C.," JOURNAL OF MATERIALS SCIENCE, No. 25, 1990.

**[0011]** 6. Jeng-Gong Duh et al., "High temperature oxidation of Fe-31Mn-9Al-xCr-0.87 C alloys (x=0, 3 and 6)," JOURNAL OF MATERIALS SCIENCE, No. 25, 1990.

**[0012]** 7. I-Hsuang Lo, advisor: T. F. Liu (one of the present inventors), "Phase Transformations in an Fe-8.8Al-30.0Mn-6.0Cr-1.0C Alloy," Thesis, National Chiao Tung University, 1990.

**[0013]** Therefore, due to the excellent mechanical properties and low density, Fe—Al—Mn alloy is applicable to various commercial products, particularly to the golf club heads.

**[0014]** To hit the golf ball higher and farther with ease and stable, it is better that alloys for golf club heads have the following characteristics: (1) low density: under the weight limitation for clubs, low-density alloy can make club large, so that the sweet zone is expand and the probability of nice shots is elevated. Also, the use of low-density alloy can save the club weight and remove the saving weight to rebuild a deeper and lower center of gravity of club to make the ball flights more stable and higher. (2) the combination of high elongation and proper strength: in order to control the direction and distance of the ball flight, alloys for club heads must be of excellent elongation and toughness, so that the contact time of ball with striking face of club is increased. In addition, heads with higher elongation is useful for adjusting loft angle within wider range in accordance with player's height; (3) high damping capacity: the alloy with higher damping capacity can absorb more vibration created by hitting a golf ball, so that the vibration is less likely to numb the hands of the golfer, and the golfer can have comfortable ball-hitting feeling and can control the ball more steadily (4) high coefficient of elasticity (Young's modulus): higher coefficient of elasticity brings longer carry; and (5) high corrosion resistance: corrosion resistance provided by the alloys themselves or surface treatments keeps club not corroded by moisture and herbicides on the grass, so that heads are kept functional and aesthetical.

**[0015]** To achieve the above requirements, attempts of use of various commercial alloys on manufacturing golf club heads have been made. Golf club heads are classified into wood and iron by functions. Generally, wood, used mainly for teeing off and stroking long carry, is hollow. In the past, woods are made of woods, commonly persimmon. With the advance of the material technology, they are replaced by heads made from metals to pursue the better performance of golf play. Commercial materials usually used for manufacturing woods currently are, for example, Ti-6Al-4V alloy,  $\beta$ -titanium, 17-4PH stainless steel, and high strength 431, 455 martensitic stainless steel. On the other hand, iron, used mainly for hitting the golf ball to target place, is character-

ized by that ball is hit a shorter but higher carry than wood, so that the controllability is more important. Commercial materials usually used for manufacturing irons currently are stainless steels, for example, 17-4PH stainless steel, 8620 steel, 1025 soft iron, 304 stainless steel, 18Ni(200) maraging steel, or titanium alloys.

**[0016]** Regarding to the above materials, some are of excellent elongation but significantly lack of strength, for example, 8620 steel and 304 stainless steel are of strength of 60 to 80 ksi and elongation of 30 to 50%. Some are of excellent strength but poor elongation, for example, 431, 455 martensitic stainless steel and 18Ni(200) maraging steel are of strength of 150 to 200 ksi and elongation of 10% or less. The development and production of titanium alloys with density of 4.5 to 4.8 g/cm<sup>3</sup>, strength of 140 to 180 ksi, and elongation of 7 to 14%, are beneficial to the design of golf club heads, but the cost is too high.

**[0017]** Accordingly, the requirements for current commercial golf club heads are: (1) density of less than 7.8 g/cm<sup>3</sup>; (2) elongation of more than 10%, (3) tensile strength of higher than 100 ksi, and (4) resistance to corrosion of 5% NaCl salt-spraying test for 24 to 48 hours or more.

**[0018]** Based on the above basic requirements, the combination of higher strength and elongation with lower density can enlarge club to expand the sweet zone and increase the controllability and the distance of the ball flight, so that the probability to hit the ball to the target is elevated. However, referring to patent documents related to Fe—Al—Mn—C alloys applied to golf club heads, only alloys disclosed in Taiwan (TW) Patent 178648 contain no chromium. Alloys disclosed in TW Patent 506845 contain titanium but optionally contain chromium, in which the coarse Ti carbides have great tendency to precipitate at grain boundaries due to a high carbon content in the alloys, so that the toughness of the alloys is reduced, and golf club heads made from the alloys are susceptible to intergranular crack in impact test. As to Fe—Al—Mn—C alloys applied to golf club heads in the other patent documents, corrosion resistance of the club is elevated by adding 5 to 9 wt % of chromium to the alloy. However, the corrosion resistance of the Cr-containing Fe—Al—Mn—C alloys is still inferior to that of 17-4PH stainless steel, high strength 431, or 455 martensitic stainless steel, which are commonly used for manufacturing golf club heads. Therefore, in order to further increase their corrosion resistance and enable clubs to pass the salt-spraying test, golf club heads made from the Cr-containing Fe—Al—Mn—C alloys still have to be subject to the electroplating process to ensure no rust on clubs in use for a period of time.

**[0019]** Chromium oxide (Cr<sub>2</sub>O<sub>3</sub>) layer is formed spontaneously on alloy surface when adding Cr element to Fe—Al—Mn—C alloys. Although the addition of Cr is able to increase the corrosion resistance of the alloys, the adherent chromium oxide layer can not be removed through common acid and activation treatments prior to the electroplating. Due to the non-conductivity of the layer acting as an insulating layer, the coating layer has a poor adhesion to the substrate and tends to spall off. However, when the acid and activation treatments employed in the electroplating process for conventional stainless steels are used to removed the chromium oxide layer on the surface of the Cr-containing Fe—Al—Mn—C alloys, the high chloride ion concentration in the acid solution attacks excessively the substrate and result in a great number pits and defects on the surface. In

consequence, the pits and defects generated during the electroplating process significantly reduce the yield rate of the products of the Fe—Al—Mn—C alloys. Therefore, in order to increase the yield rate, it is necessary to develop a new Fe—Al—Mn—C alloy with excellent mechanical properties to avoid generating the pits and defects during the electroplating process.

#### SUMMARY OF THE INVENTION

**[0020]** Depending on the theory of the alloy design and the study of the microstructures in the Fe—Al—Mn—C alloys by means of the transmission electron microscopy(TEM), the present inventors has developed a low-density Fe—Al—Mn—C alloy with high strength and ductility and the method of making. The alloy has a density of 6.6 to 6.9 g/cm<sup>3</sup>, an elongation of 25 to 70%, and a tensile strength of 100 to 190 ksi. In particular, the use of the alloy on manufacturing golf club heads is capable of reducing the pits and defects generated during the electroplating process of the heads, so that the yield rate of the products is remarkably increased.

**[0021]** The effects of the elements added to the alloy are described in the following:

**[0022]** 1. Mn: Manganese is one of austenite formers. Since the austenite phase has a face-centered cubic structure, the ductility of the alloy increases with increasing the volume fraction of the austenite phase. To obtain a superior ductility, the alloy of the present invention should contain at least 15 wt. % Mn. However, when the alloy contains more than 33 wt. % Mn, the precipitation of the  $\beta$ -Mn starts to appear and then deteriorates the ductility of the alloy. Therefore, the Mn content should be controlled to be equal to or greater than 15 wt. % but lower than or equal to 33 wt. %.

**[0023]** 2. Al: Aluminum is not only a stabilizing element for ferrite, but also an essential element for (Fe,Mn)<sub>3</sub>AlC<sub>x</sub> superlattice carbides. Thus, the added amount of Al strongly affects the formation and amount of (Fe,Mn)<sub>3</sub>AlC<sub>x</sub> carbides. The amount of (Fe,Mn)<sub>3</sub>AlC<sub>x</sub> carbides formed in austenitic matrix is too low when the added amount of Al is less than 6 wt %, and desired strength of alloy is not obtained. However, when more than 10 wt % Al is added, ferrite phase is formed and disordered ferrite phase (bcc) tends to transform into brittle D0<sub>3</sub> ordered phase during heat treatments. Besides, due to very low saturation concentration of carbon in ferrite phase, large (Fe,Mn)<sub>3</sub>AlC<sub>x</sub> carbides can be observed to precipitate at the grain boundaries. This does not elevate the strength of the alloy and, on the contrary, sharply reduces ductility of alloy. Thus, the brittle intercrystalline breakage is formed. Therefore, the Al content should be controlled to be equal to or greater than 6 wt. % but lower than or equal to 10 wt %.

**[0024]** 3. C: Carbon is not only a strong austenite stabilizer, but also a constituent element forming (Fe, Mn)<sub>3</sub>AlC<sub>x</sub> superlattice carbides.

**[0025]** Similarly, the amount of (Fe,Mn)<sub>3</sub>AlC<sub>x</sub> carbides formed in austenite phase is too low when the added amount of C is less than 0.6 wt %, and desired strength of alloy can not be obtained. However, when more than 1.2 wt % C is added, the carbides are observed to have large sizes and start to precipitate at grain boundaries. This makes the alloy susceptible to intergranular fracture and ductility is sharply

reduced. Therefore, the C content should be controlled to be equal to or greater than 0.6 wt. % but lower than or equal to 1.2 wt %.

**[0026]** 4. Si: Addition of 0.1 wt % or more of silicon enhances  $(\text{Fe,Mn})_3\text{AlC}_x$  carbides to finely and coherently form in the austenite phase through spinodal decomposition during quenching so that the strength of alloy is raised. Also, addition of Si increases fluidity of liquid alloy and facilitates casting of alloy. However, Si is not only a strong ferrite former but also an element to enhance the formation of the brittle  $\text{DO}_3$  ordered in Fe—Mn—Al alloys. When the Si content is more than 1.0 wt %, brittle  $\text{DO}_3$  ordered phase is formed, and the ductility of alloy is seriously deteriorated. Therefore, the Si content should be controlled to be equal to or greater than 0.1 wt. % but lower than or equal to 1.0 wt %.

**[0027]** 5. Mo: The present inventors found that the addition of molybdenum to the Fe—Mn—Al alloys can increase the strength by the mechanism of the solid-solution strengthening. However, when the Mo content is more than 1.5 wt %, molybdenum carbides like  $\text{M}_2\text{C}$ ,  $\text{M}_{23}\text{C}_6$  and  $\text{M}_6\text{C}$  are observed to precipitate in the alloy. The presence of the molybdenum carbides leads to the lack of carbon in the vicinity of the carbides, and makes the austenite phase unstable and then tends to transform into the less-ductility ferrite phase. Therefore, the Mo content should be controlled to be not more than 1.5 wt %.

**[0028]** To achieve the above objects, the present inventors has focused on ratio and composition of various added elements and develop a high strength and high toughness alloy with low density, which comprises 15 to 33 wt % of manganese, 6 to 10 wt % of aluminum, 0.6 to 1.2 wt % of carbon, 0.1 to 1.0 wt % of silicon, with up to 1.5 wt % of molybdenum, and the balance of iron.

**[0029]** The present alloy, which comprises 15-33 wt % of manganese, 6-10 wt % of aluminum, 0.6-1.2 wt % of carbon, 0.1-1.0 wt % of silicon, with up to 1.5 wt % of molybdenum, and the balance of iron, can be optionally solution-heat-treated at 950 to 1200° C. for 0.5 to 10 hours, and then aged at 500 to 700° C. for up to 24 hours, or without any heat treatment.

**[0030]** The present alloy, which comprises 15-33 wt % of manganese, 6-10 wt % of aluminum, 0.6-1.2 wt % of carbon, 0.1-1.0 wt % of silicon, with up to 1.5 wt % of molybdenum, and the balance of iron, can be subject to hot-working at 800 to 120° C. or cold working. The plastically worked alloy can be optionally solution-heat-treated at 950 to 1200° C. for 0.5 to 10 hours, and then aged at 500 to 700° C. for up to 24 hours, or without any heat treatment.

#### BRIEF DESCRIPTION OF THE DRAWING

**[0031]** FIG. 1 shows the comparison of the compositions between alloys made by the present invention and the disclosed Fe—Mn—Al based alloys in the prior arts.

#### DETAILED DESCRIPTION OF THE INVENTION

**[0032]** For a further understanding of the compositions and mechanical properties, in addition, objects, technical description, features, and effects of the present invention by

those familiar in this field, the present invention is described with reference to the following embodiments, figures and tables.

**[0033]** The present invention relating to a high strength and high toughness alloy with a low density that is particularly useful for golf club heads, which comprises 15 to 33 wt % of manganese, 6 to 10 wt % of aluminum, 0.6 to 1.2 wt % of carbon, 0.1 to 1.0 wt % of silicon, with up to 1.5 wt % of molybdenum, and the balance of iron.

**[0034]** Following is a detailed description with reference to embodiments. As shown in FIG. 1, Alloys No.1-7 represent the alloys of the present invention, and No.8-13 represent the disclosed Fe—Mn—Al alloys applied to golf club heads in the prior arts which are listed as comparative examples as references to the present invention.

**[0035]** Alloy No.1: A preferable example of the invention, which comprises 27.8 wt % of manganese, 8.8 wt % of aluminum, 0.95 wt % of carbon, 0.28 wt % of silicon, and the balance of iron, is melted in induction furnace and cast in pre-heated de-waxed shell mold of golf club heads. After shell mold is cooled, procedures like shell shaking, gate cutting, sand blasting, grinding, welding, drilling, electroplating and surface treatment and finishing are performed. The golf club head casting has excellent properties of density of 6.70 g/cm<sup>3</sup>, elongation of 38.6%, and tensile strength of 122.5 ksi, without plastic working (like forging and rolling) and any heat treatment. The producing of pits on the heads is remarkably reduced after electroplating.

**[0036]** Alloy No.2: Another preferable example of the invention, which comprises 30.3 wt % of manganese, 8.8 wt % of aluminum, 1.15 wt % of carbon, 0.16 wt % of silicon, 1.05 wt % of molybdenum, and the balance of iron, is melted in induction furnace and cast in pre-heated de-waxed shell mold of golf club heads. After shell mold is cooled, procedures like shell shaking, channel gate cutting, sand blasting, grinding, welding, drilling, electroplating and surface treatment and finishing are performed. Due to the addition of 1.05 wt. % Mo, the tensile strength of the golf club head is raised by 8 to 10 ksi without a obvious decrease in ductility. Consequently, the golf club head has excellent properties of density of 6.79 g/cm<sup>3</sup>, elongation of 35.1%, and tensile strength of 130.7 ksi, without plastic working (like forging and rolling) and any heat treatment. The producing of pits on the heads is remarkably reduced after electroplating.

**[0037]** Alloy No.3: Another preferable example of the invention, which comprises 17.5 wt % of manganese, 6.2 wt % of aluminum, 1.08 wt % of carbon, 0.15 wt % of silicon, and the balance of iron, is melted in induction furnace and cast in pre-heated de-waxed shell mold of golf club heads. The solution heat treatment of head casting is performed at 1100° C. under vacuum for 4 hours to increase the ductility. Accordingly, the golf club head has excellent properties of density of 6.73 g/cm<sup>3</sup>, elongation of 45.4%, and tensile strength of 116.8 ksi, without plastic working (like forging and rolling). The producing of pitting caves on the heads is remarkably reduced after electroplating.

**[0038]** Alloy No.4: Another preferable example of the invention, which comprises 24.9 wt % of manganese, 7.3 wt % of aluminum, 1.05 wt % of carbon, 0.17 wt % of silicon, and the balance of iron, is melted in induction furnace and cast in pre-heated de-waxed shell mold of golf club heads. The solution heat treatment of head casting is performed at 1100° C. under vacuum for 2 hours to increase the ductility. Accordingly, the golf club head has excellent properties of

density of 6.73 g/cm<sup>3</sup>, elongation of 64.5%, and tensile strength of 120.1 ksi, without plastic working (like forging and rolling). The producing of pits on the heads is remarkably reduced after electroplating.

**[0039]** Alloy No.5: Another preferable example of the invention, which comprises 29.1 wt % of manganese, 8.5 wt % of aluminum, 0.62 wt % of carbon, 0.26 wt % of silicon, and the balance of iron, is melted in induction furnace and cast in pre-heated de-waxed shell mold of golf club heads. The golf head castings are subject to solution heat treatment at 1050° C. under vacuum for 2 hours, and then aged at 600° C. for 2 hours. Accordingly, the golf club head has excellent properties of density of 6.70 g/cm<sup>3</sup>, elongation of 36.9%, and tensile strength of 148.7 ksi, without plastic working (like forging and rolling). The producing of pits on the heads is remarkably reduced after electroplating.

**[0040]** Alloy No.6: Ingot of another preferable example of the invention, which comprises 32.1 wt % of manganese, 9.0 wt % of aluminum, 0.78 wt % of carbon, 0.31 wt % of silicon, and the balance of iron, is hot rolled or forged to be a rod or plate with an appropriate dimension. Then, the rod is taken to a series of the precision mold forging process to produce forged golf club heads. For the plate, it is directly pressed to make the faces of the golf club heads and then welded together with the club bodies. Subsequently, the golf heads are solution-heat-treated at 1050° C. under vacuum for 2 hours, and then aged at 600° C. for 2 hours. Accordingly, the golf club head has excellent properties of density of 6.67 g/cm<sup>3</sup>, elongation of 36.1%, and tensile strength of 189.5 ksi. The producing of pits on the heads is remarkably reduced after electroplating.

**[0041]** Alloy No.7: Ingot of another preferable example of the invention, which comprises 31.6 wt % of manganese, 8.7 wt % of aluminum, 1.10 wt % of carbon, 0.56 wt % of silicon, and the balance of iron, is hot rolled or forged to be a rod or plate with an appropriate dimension. Then, the rod is taken to a series of the precision mold forging process to produce forged golf club heads. For the plate, it is directly pressed to make the faces of the golf club heads and then welded together with the club bodies. Subsequently, the golf heads are solution-heat-treated at 1050° C. under vacuum for 2 hours, and then aged at 500° C. for 6 hours. Accordingly, the golf club head has excellent properties of density of 6.65 g/cm<sup>3</sup>, elongation of 30.8%, and tensile strength of 178.2 ksi. The producing of pits on the heads is remarkably reduced after electroplating.

**[0042]** Alloy No.8: An Fe—Mn—Al based alloy comprising 22 to 36 wt % of manganese, 6 to 8 wt % of aluminum, 1.5 to 2.0 wt % of carbon, 1.0 to 1.5 wt % of molybdenum, and the balance of iron, can obtain required mechanical properties only after solution treatment at 1030 to 1050° C. for 1 to 2 hours, and aging treatment at 450-550° C. for 1-2 hours. Additionally, since the alloy contains a higher carbon content of 1.5 to 2.0 wt. %, the carbides have a high tendency to precipitate and grew along grain boundaries to make the alloy sensitive to the intergranular fracture. (disclosed in the TW Patent 178648, Making Method of Fe—Mn—Al Alloy Fine Casting).

**[0043]** Alloy No.9: Casting of alloy comprising 22 to 28 wt % of manganese, 6.5 to 8 wt % of aluminum, 5.0 to 6.0 wt % of chromium, 0.9 to 1.1 wt % of carbon, 0.2 to 1.5 wt % of silicon, 1.0 to 1.2 wt % of molybdenum, 0.9 to 1.1 wt % of copper, 0.02-0.04 wt % of niobium, and the balance of iron, has to be subject to homogenization heat treatment in

atmosphere furnaces, atmosphere controlled furnaces, or vacuum furnaces (disclosed in the TW Patent 185568, Making Method for Finely Casting Rust-Preventing Alloy).

**[0044]** Alloy No.10: An alloy comprising 25 to 31 wt % of manganese, 6.3 to 7.8 wt % of aluminum, 5.5 to 9.0 wt % of chromium, 0.65 to 0.85 wt % of carbon, and the balance of iron, is subject to hot forging at temperatures of 800 to 1050° C. and heat treatment at temperatures of 980 to 1080° C. for 1 to 24 hours. Further, 0.8 to 1.5 wt % of silicon and 2.0 to 5.0 wt % of titanium can be added, as well as 0.5 to 1.0 wt % of molybdenum (disclosed in the US Patent 20030077479, Low Density and High Ductility Alloy Steel for a Golf Club Head).

**[0045]** Alloy No.11: An alloy comprising 28.0 to 31.5 wt % of manganese, 7.8 to 10.0 wt % of aluminum, 0.9 to 1.10 wt % of carbon, 0.35 to 2.5 wt % of titanium, and the balance of iron, is subject to hot forging at temperatures of 900 to 1100° C. and heat treatment at temperatures of 950 to 1270° C. for 1 to 24 hours. Further, 5.0 to 7.0 wt % of chromium or 0.8 to 1.5 wt % of silicon can be added (disclosed in the US Patent 20030082067, Low-Density Iron Based Alloy for a Golf Club Head).

**[0046]** Alloy No.12: An alloy comprising 25 to 31 wt % of manganese, 5 to 7 wt % of chromium, 7 to 10 wt % of aluminum, 0.9 to 1.1 wt % of carbon, and the balance of iron, is subject to plastic working (cold and hot forging), and then heat treatment at temperatures of 950 to 1270° C. for 1 to 24 hours. Subsequently, it is subject to hot forging at temperature of 800-1050° C., and heat treatment at temperatures of 980 to 1080° C. for 1 to 4 hours and then at temperatures of 500 to 650° C. for 4 to 8 hours. Further, 0.8 to 1.5 wt % of silicon, 2 to 5 wt % of chromium, or 0.5 to 1.0 wt % of molybdenum can be added (disclosed in the U.S. Pat. No. 584,568, Low Density Iron Based Alloy for a Golf Club Head).

**[0047]** Alloy No.13: An alloy comprising 23.0 to 30.0 wt % of manganese, 6.3-10.0 wt % of aluminum, 0.8 to 1.05 wt % of carbon, 5.0 to 9.0 wt % of chromium, 0.2 to 10.0 wt % of cobalt, and the balance of iron, is subject to hot forging at temperatures of 1000 to 1050° C., and then heat treatment at temperature of 1030 to 1080° C. for 15 to 60 minutes and at temperatures of 450 to 850° C. for 4 to 24 hours to manufacture golf club head. Further, 0.6 to 1.0 wt % of silicon and 0.2 to 0.4 wt % of nitrogen can be added (disclosed in the TW Patent I235677, Low Density and High Ductility Fe-based Alloy for a Golf Club Head).

**[0048]** Therefore, the high strength and high toughness alloy with low density provided by the present invention is useful for manufacturing forging, casting or the combination of both types of golf club heads. The manufactured heads have mechanical properties of density of 6.6-6.9 g/cm<sup>3</sup>, tensile strength of 100 to 190 ksi, and elongation of 25 to 70%. Since the alloy of the present invention does not contain chromium conventionally added to the Fe—Mn—Al based alloys for golf club heads in the prior arts, pits are remarkably reduced after electroplating the club heads made from the present alloy.

**[0049]** In addition, golf club heads made from the present alloy have superior characteristics and advantages, described as following.

**[0050]** 1. Low density: golf club head made from the present alloy is 15 to 23% larger than that made from 17-4PH stainless steel, which expands the sweet zone to elevate the probability of properly hitting the ball. Also,

the use of low-density alloy can save the club weight and remove the saving weight to rebuild a deeper and lower center of gravity of club to elevate the stability and carry while playing golf.

**[0051]** 2. High damping ratio (high damping capacity): according to the test result of the present invention, the damping capacity of the present alloy is 1.5 to 3 times higher than those of the conventional alloys used in golf club heads, such as Ti-6Al-4V Titanium alloy and 17-4PH stainless steel. A golf club head with high damping capacity enables a better controllability and can absorb more vibration while hitting the golf ball, so that players can have a more comfortable feeling.

**[0052]** 3. High Young's modulus: according to the test result of the present invention, the present alloy has a higher Young modulus than Ti-6Al-4V alloy and 17-4PH stainless steel. The alloy with a higher Young's modulus can bring a longer flight distance of golf ball.

**[0053]** 4. Low cost: according to the practical mass production of the golf club heads made from the present alloy, the pits generated on the surface of the Fe—Mn—Al based alloy during the electroplating process of the heads are remarkably reduced. Therefore, the defect rate of the product is significantly decreased so that the cost is obviously reduced.

**[0054]** As described above, the present invention develops a new alloy with characteristics of low density, high strength, high toughness and high damping capacity. In particular, the use of the present alloy can efficiently prevent the pits and defects generated during the electroplating process.

**[0055]** The present invention is disclosed above with reference to the preferred embodiments; however, the embodiments are not used as limitation of the present. It is appreciated to those in this field that the variation and modification directed to the present invention not apart from the spirit and scope thereof can be made, and the scope of the present invention is covered in the attached claims.

1. A iron-based alloy comprising 15 to 33 wt % of manganese, 6 to 10 wt % of aluminum, 0.6 to 1.2 wt % of carbon, 0.1 to 1.0 wt % of silicon, and the balance of iron.

2. The alloy according to claim 1, which further comprises up to 1.5 wt % of molybdenum.

3. The alloy according to claim 1, wherein the alloy has a density of 6.6 to 6.9 g/cm<sup>3</sup>, an elongation of 25 to 70%, and a tensile strength of 100 to 190 ksi.

4. The alloy according to claim 1, which is characterized by remarkably reducing pits generated during the electroplating process.

5. A method of making an iron-based alloy comprising incorporating 15 to 33 wt % of manganese, 6 to 10 wt % of

aluminum, 0.6 to 1.2 wt % of carbon, 0.1 to 1.0 wt % of silicon, and the balance of iron through a melting process.

6. The method according to claim 5, wherein the alloy further comprises up to 1.5 wt % of molybdenum through a melting process.

7. The method according to claim 5, wherein the melting process is atmospheric melting.

8. The method according to claim 5, wherein the alloy has a density of 6.6 to 6.9 g/cm<sup>3</sup>, an elongation of 25 to 70%, and a tensile strength of 100 to 190 ksi.

9. An alloy for golf club heads comprising 15 to 33 wt % of manganese, 6 to 10 wt % of aluminum, 0.6 to 1.2 wt % of carbon, 0.1 to 1.0 wt % of silicon, and the balance of iron.

10. The alloy according to claim 9, which further comprises up to 1.5 wt % of molybdenum.

11. The alloy for golf club heads according to claim 9, wherein the alloy has a density of 6.6 to 6.9 g/cm<sup>3</sup>, an elongation of 25 to 70%, and a tensile strength of 100 to 190 ksi.

12. The alloy according to claim 9, which is characterized by remarkably reducing pits generated during the electroplating process of the golf club heads.

13. A method of making an alloy for manufacturing golf club heads comprising 15 to 33 wt % of manganese, 6 to 10 wt % of aluminum, 0.6 to 1.2 wt % of carbon, 0.1 to 1.0 wt % of silicon, and the balance of iron through a melting process.

14. The method of making an alloy for golf club heads according to claim 13, wherein the alloy further comprises up to 1.5 wt % of molybdenum through a melting process.

15. The method of making an alloy for golf club heads according to claim 13, wherein the melting process is atmospheric melting.

16. The method of making an alloy for golf club heads according to claim 13, wherein the alloy has a density of 6.6 to 6.9 g/cm<sup>3</sup>, an elongation of 25 to 70%, and a tensile strength of 100 to 190 ksi.

17. The method according to claim 5, wherein the melting process is vacuum melting.

18. The method according to claim 5, wherein the melting process is reduction melting.

19. The method of making an alloy for golf club heads according to claim 13, wherein the melting process is vacuum melting.

20. The method of making an alloy for golf club heads according to claim 13, wherein the melting process is reduction melting.

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