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(54) **LOW-DENSITY HIGH-TOUGHNESS ALLOY AND THE FABRICATION METHOD THEREOF**

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(57) **ABSTRACT**

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The present invention discloses a low-density high-toughness alloy and the fabrication method thereof. The alloy of the present invention consists essentially of: by weight percent, equal to or greater than 23% but lower than or equal to 33% manganese, equal to or greater than 8.1% but lower than or equal to 9.8% aluminum, equal to or greater than 3% but lower than or equal to 7.8% chromium, equal to or greater than 0.6% but lower than or equal to 1.2% carbon, equal to or greater than 0.1% but lower than or equal to 0.24% silicon and the balance of iron. The golf-club head made from the abovementioned alloy can obtain superior elongation, strength, damping capacity, and corrosion resistance even without any heat treatment, or any hot/cold working, such as forging and rolling; therefore, the fabrication cost thereof can be obviously reduced.

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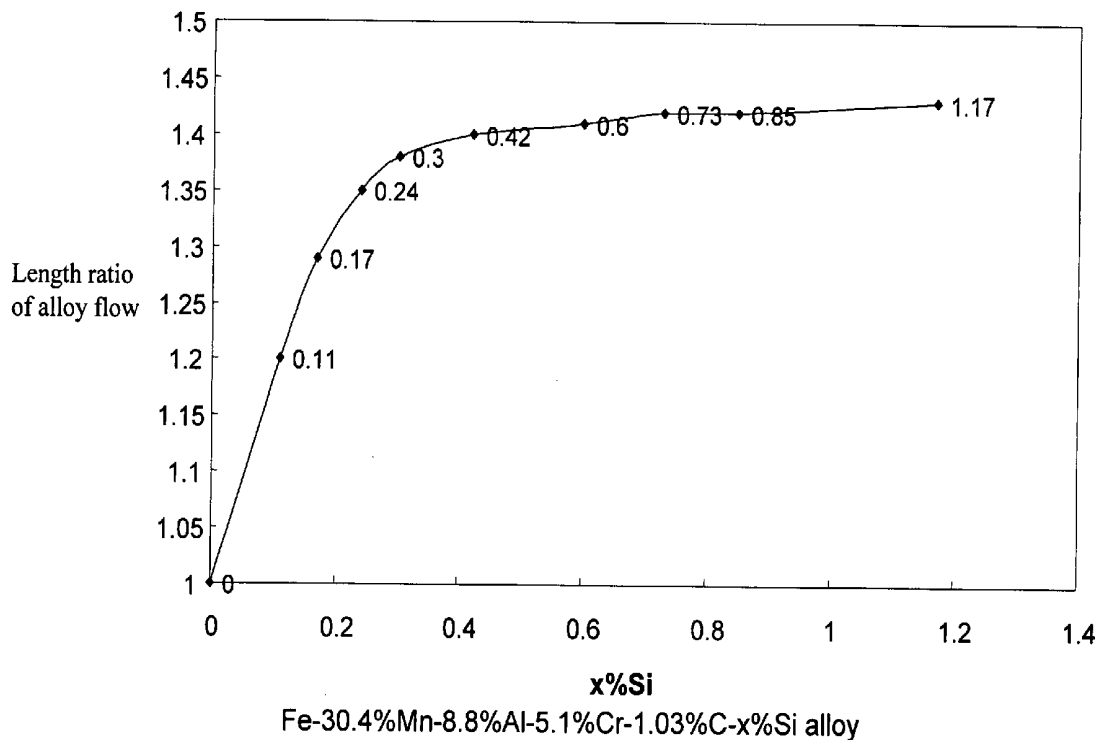
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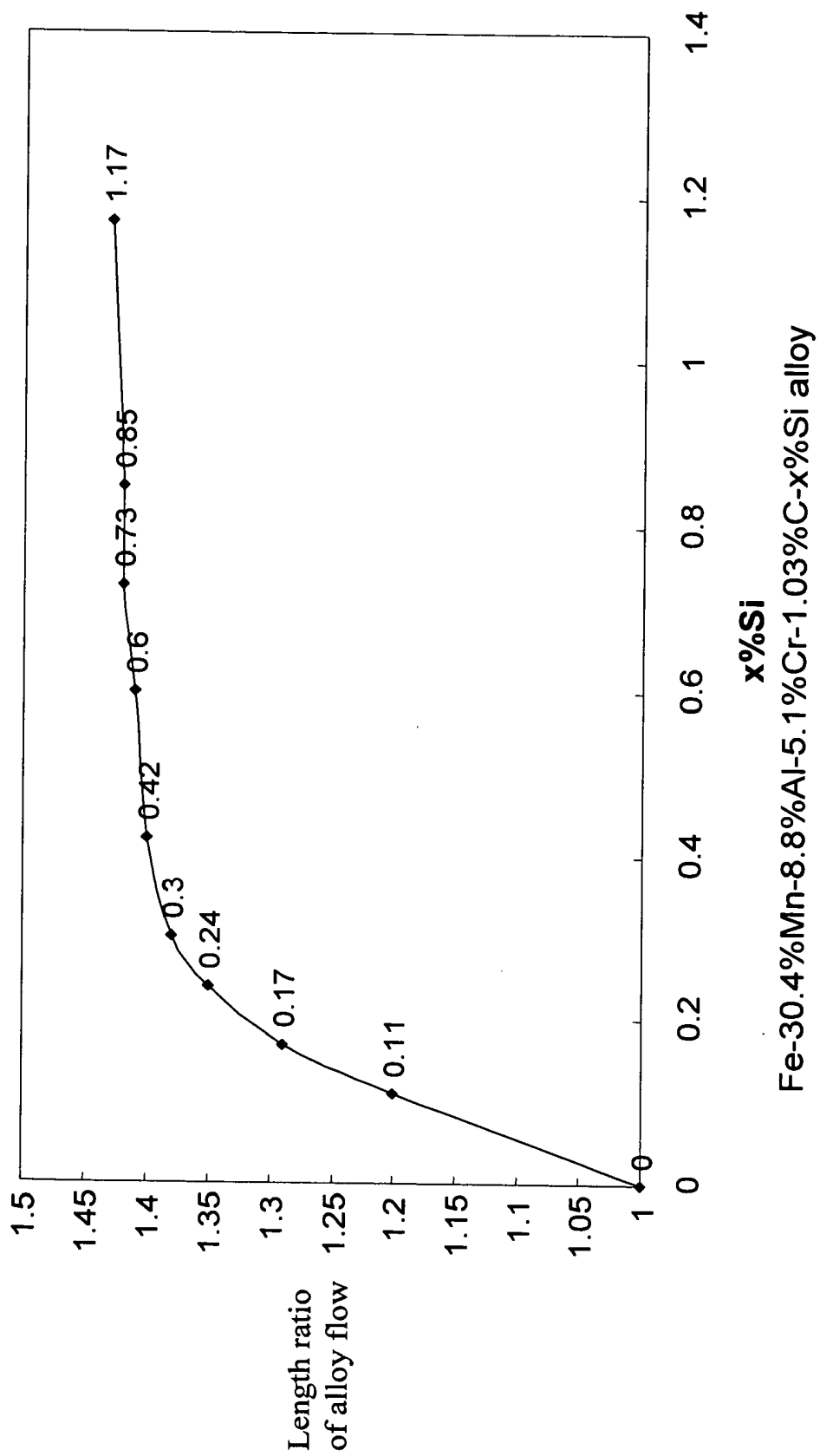


Fig. 1

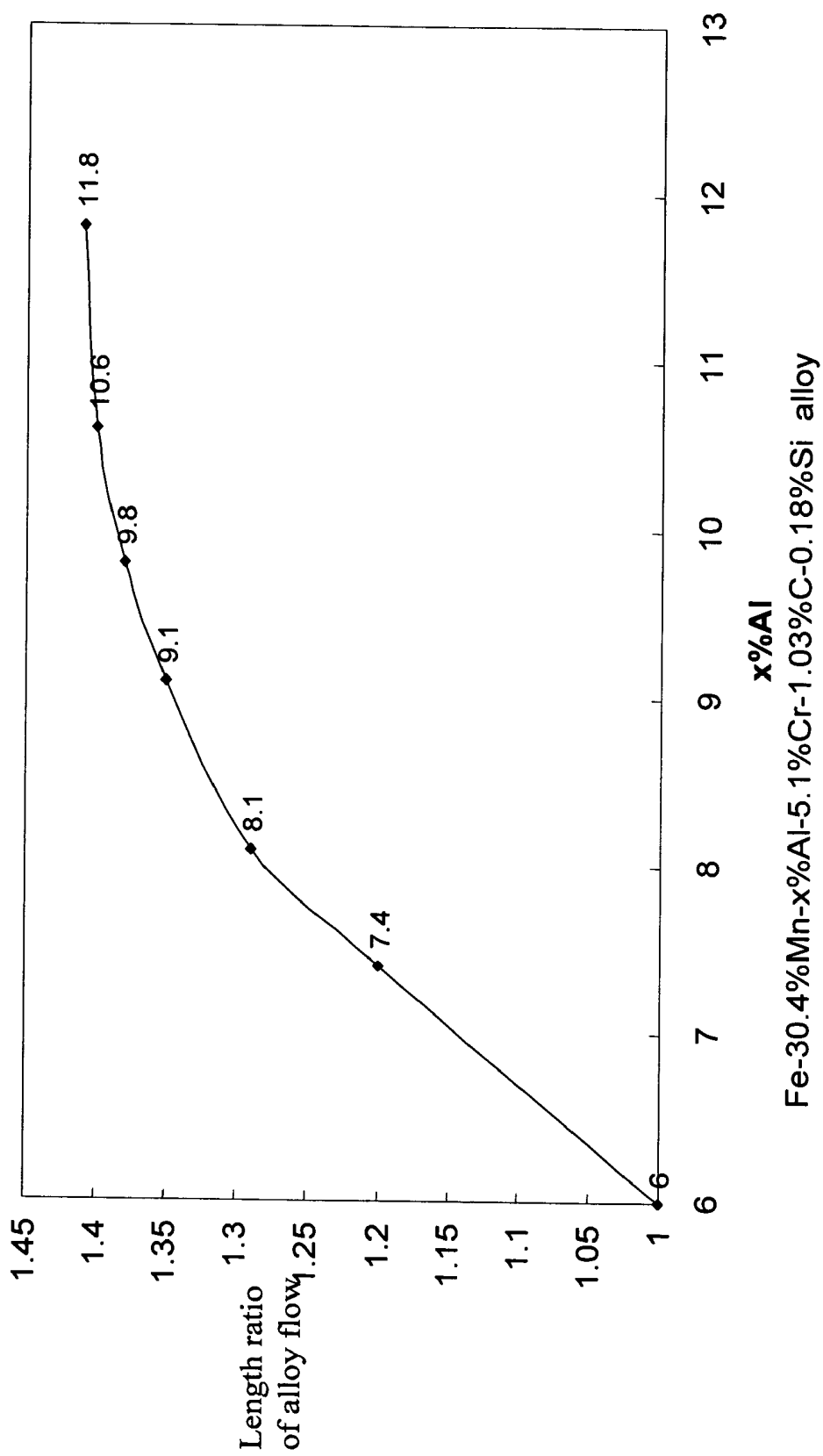


Fig. 2

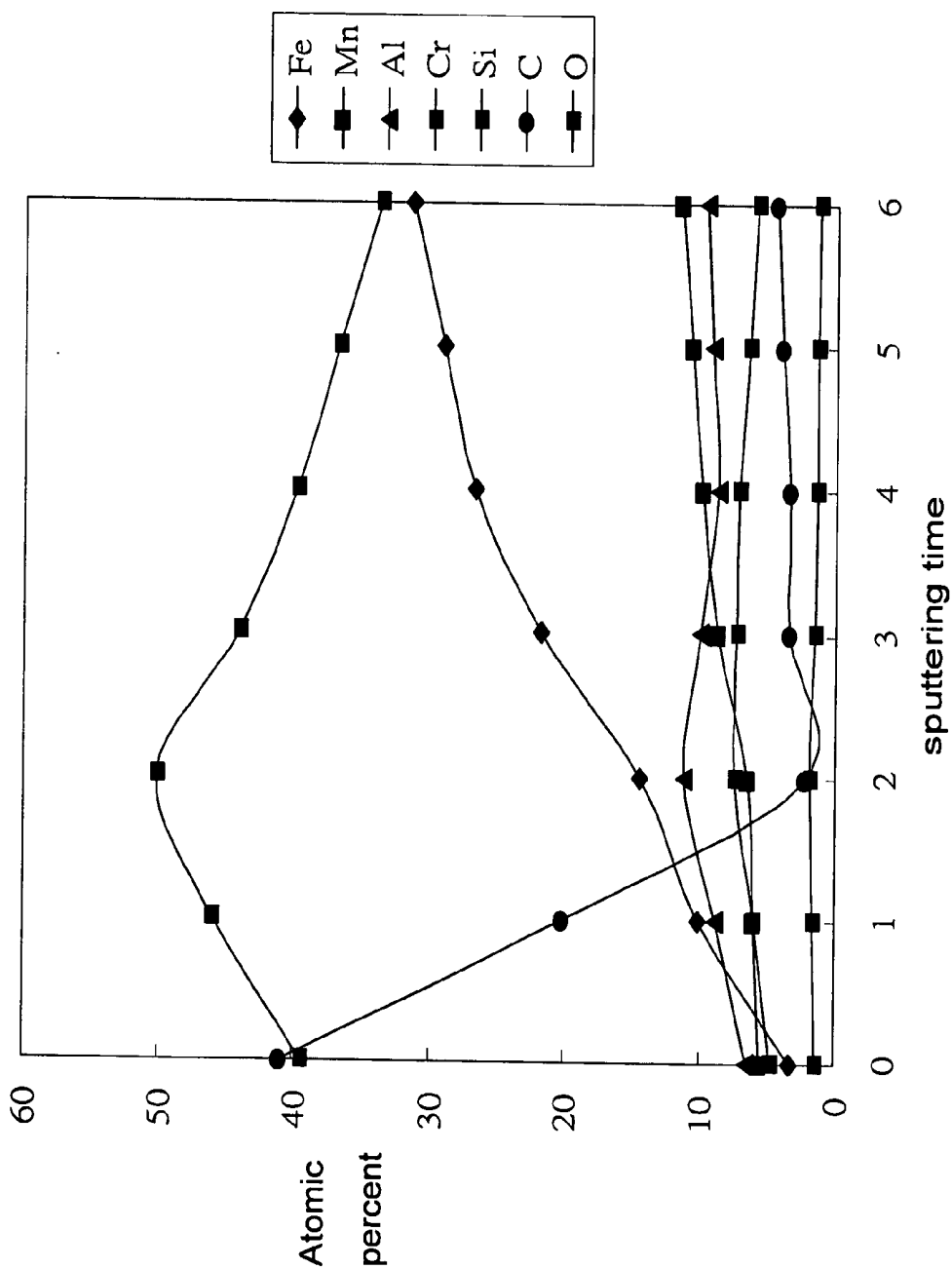


Fig. 3

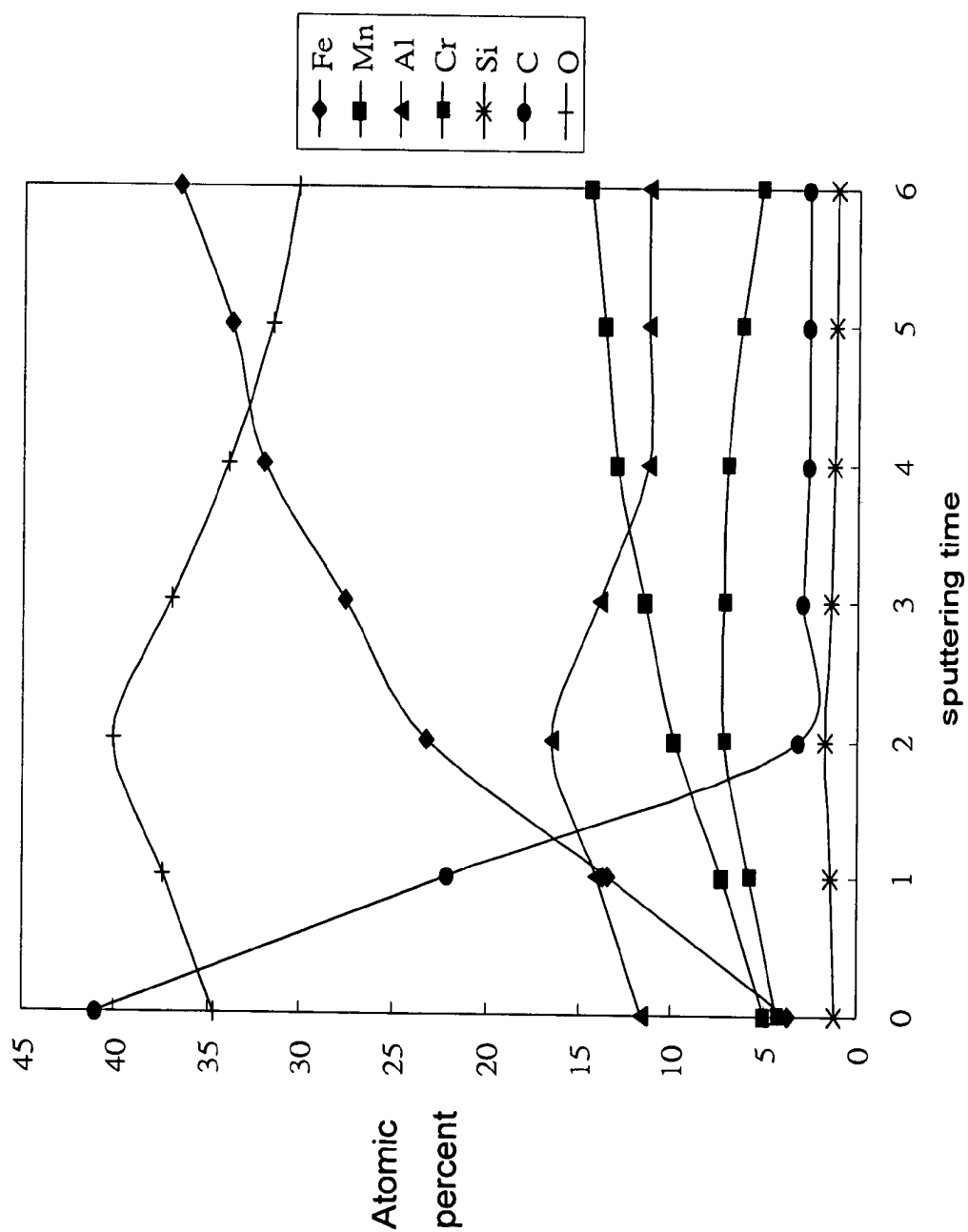


Fig. 4

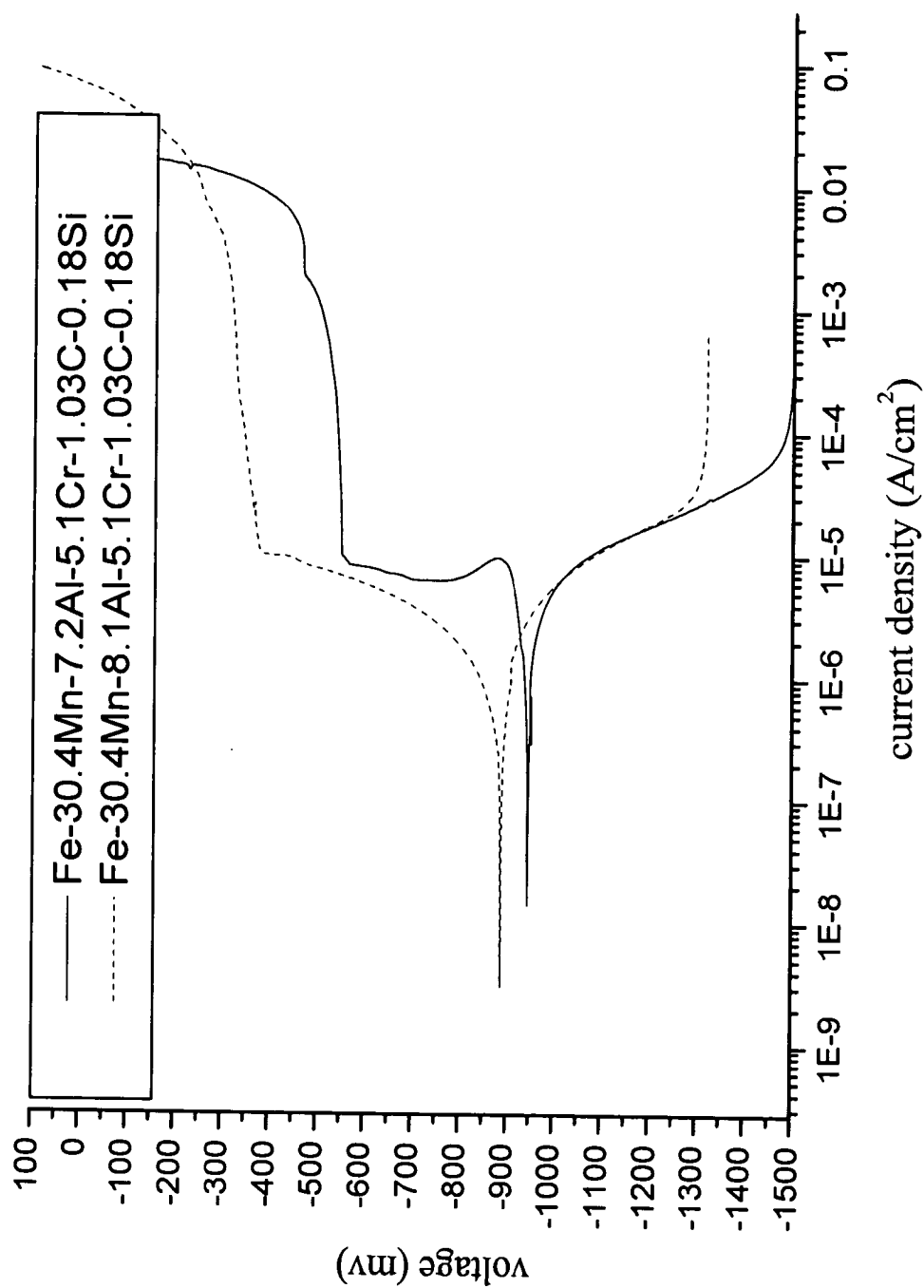


Fig. 5

LOW-DENSITY HIGH-TOUGHNESS ALLOY AND THE FABRICATION METHOD THEREOF

BACKGROUND OF THE INVENTION

[0001] 1. Field of the Invention

[0002] The present invention relates to a low-density alloy, particularly to a low-density alloy for use of making golf-club heads with superior elongation, strength, damping capacity, and corrosion resistance generated without any heat treatment and plastic deformation process, including hot working, and cold working.

[0003] 2. Description of the Related Art

[0004] To provide a better ball-hitting feeling for the golfers, and to enable the golfer to hit the ball farther and more stably (i.e. longer ball-contacting time, higher ball-controlling ability, and lower vibration), many commercial materials have been applied to golf-club heads, such as 8620 soft iron, 304 austenitic stainless steel, 17-4PH precipitation-hardening stainless steel, AISI431/AISI455 high-strength martensitic stainless steel, 18Ni(200) maraging steel, Ti-6Al-4V alloy, and SP-700 titanium alloy. Among those materials, some have superior ductility, but the strength thereof is pretty insufficient; for example, 8620 soft iron and 304 austenitic stainless steel have an elongation as high as about 50% but have a tensile strength of only about 80 ksi. Some have very high strength, but the ductility thereof is pretty low; for example, AISI431/AISI455 high-strength martensitic stainless steel and 18Ni(200) maraging steel have a tensile strength as high as 150~200 ksi but have an elongation of only 10% or below. According to the current design principles of golf-club heads, the ideal material for the golf-club head should have the following characteristics: (1) low density: under the requirement that the golf-club heads of a specified number should be equal to a specified weight, the golf-club head using a low-density material can have a larger volume; therefore, the ball-striking sweet zone can be enlarged, and the probability of utilizing the correct region to hit the ball increases; further, the low density golf-club head material can also increase the design flexibility of the balance weight, lower the gravitational center of the golf-club head, and then increase the stability and the swing force of the ball-striking actions, so that balls can be hit farther and more accurately; (2) appropriate combination of ductility and strength: the loft angle between the shaft and the striking face may be adjusted according to the height of the golfer; the higher the ductility of the golf-club head material, the larger the allowable range of adjusting the loft angle; further, the higher the ductility, the longer the time that the golf ball contacts the striking face, and thus, the flying trajectory of the golf ball can be more easily controlled, and the ball-controlling ability is promoted; (3) high damping ratio: the material of high damping capacity can absorb the vibration created by hitting a ball, so that the vibration is less likely to numb the hands of the golfer, and the golfer can have a better ball-hitting feeling and can control the golf ball more steadily; (4) high elastic modulus (Young's modulus): the higher the elastic modulus, the longer the flight distance of the golf ball; (5) high corrosion resistance: high corrosion resistance makes the golf-club head less likely to rust when it is used in humidified and herbicide-containing lawn; thus, the function and appearance of the golf-club head can be maintained, and the design flexibility of golf-club heads can also be promoted.

[0005] Therefore, a Fe—Mn—Al—C-based low-density high-toughness alloy has come to the attention of the golf world. The development history of the Fe—Mn—Al—Cr—C alloy and its applications to golf-club heads will be described below.

[0006] In the Age of Cold War, nickel and chromium are resources of high strategic and economical value; however, the conventional Ni—Cr-based stainless steel comprises high proportion of Ni and Cr; furthermore, the chromium and nickel mines are not common in the Western World but rich in the Republic of Zimbabwe and the Republic of South Africa. Owing to strategic and economical considerations, researchers began to develop Ni/Cr-free stainless steel and tried to replace Cr and Ni with Mn and Al; therefore, the Fe—Mn—Al alloy was developed then. From many researches, it is found: since the Fe—Mn—Al alloy has a protective high-temperature-durable aluminum-oxide layer formed on the surface, the Fe—Mn—Al alloy has better oxidation resistance at high temperature than the traditional stainless steel, and the weight gain of the Fe—Mn—Al alloy is also much less than that of the conventional stainless steel; however, in the environment of sea water or corrosive liquid, the corrosion-resistance of the Fe—Mn—Al alloy is inferior to that of the conventional stainless steel.

[0007] Excluding the case that the Fe—Mn—Al alloy is used as a substitute for stainless steel, a series of Fe—Mn—Al—C-based high-strength and high-ductility alloys has been developed by many specialists and scholars for the last two decades; the properties of those Fe—Mn—Al—C alloys are clearly described in the following papers.

[0008] 1. G. L. Kayak, "Fe—Mn—Al Precipitation-Hardening Austenitic Alloys", *Metal Science and Heat Treatment*, Vol. 2, 1969, P. 95

[0009] 2. M. F. Alekseenko, et al., "Phase Composition Structure and Properties of Low-Density Steel 9G28Yu9MVB", *Metal Science and Heat Treatment*, Vol. 14, 1972, P. 187

[0010] 3. G. S. Krivonogov, et al., "Phase Transformation Kinetics in Steel 9G28Yu9MVB", *Phys. Met. & Metallog*, Vol. 4, 1975, P. 86

[0011] 4. L. I. Lysak, et al., "Structural and Phase Change in Steel 9G28Yu9MVB During Aging", *Metallogizika*, Vol. 59, 1975, P. 29

[0012] 5. Charles, et al., "New Cryogenic Materials: Fe—Mn—Al Alloys", *Metal Progress*, May, 1981, P. 71

[0013] 6. C. J. Altstetter, et al., "Processing and Properties of Fe—Mn—Al Alloys", *Materials Science and Engineering*, Vol. 82, 1986, P. 13

[0014] 7. K. H. Ham, et al., "The Evidence of Modulated Structure in Fe—Mn—Al—C Austenitic Alloys", *Scripta Metal.*, Vol. 20, 1986, P. 33

[0015] 8. P. J. James, "Precipitation of the Carbide (Fe, Mn)₃AlC in an Fe—Al Alloy", *J. Iron & Steel Inst.*, January 1969, P. 54

[0016] From surveying the abovementioned papers, it is found: after the processes of a plastic working (such as forging and rolling), a solid-solution heat treatment at the temperature of 950~1200° C., a fast quenching, and then an aging heat treatment at the temperature of 450~750° C., the

Fe-(28~35) wt. % Mn-(4.9~1) wt. % Al-(0.5~2.0) wt. % C-based alloy becomes a high-strength and high-ductility alloy having an austenitic-matrix structure, a density of 6.6~6.8 g/cm³, a tensile strength of 100~180 ksi, a yield strength of 90~160 ksi, and an elongation of 25~65%.

[0017] In order to improve the corrosion resistance, 2.98~6 wt. % of Cr and 0.9~1.03 wt. % of Mo may be further added into the abovementioned Fe—Mn—Al—C-based alloy; the corrosion resistance thereof has been discussed in detailed in the following papers.

[0018] 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. 20, No. 3, March 1989

[0019] 2. Jeng-Gong Duh, et al., "Microstructural development in the oxidation-induced phase transformation of Fe—Al—Cr—Mn—C alloys", JOURNAL OF MATERIALS SCIENCE, Vol. 23, 1989

[0020] 3. J. G. Duh, et al., "Nitriding behavior in Fe—Al—Mn—Cr—C alloys at 1000-1100° C.", JOURNAL OF MATERIALS SCIENCE, Vol. 28, 1993

[0021] 4. S. C. Chang, et al., "Environment-Assisted Cracking of Fe-32% Mn-9% Al Alloys in 3.5% Sodium Chloride Solution", J. CORROSION, Vol. 51, 1995

[0022] 5. J. G. Duh, et al., "Nitriding Kinetics of Fe—Al—Mn—Cr—C alloys at 1000° C.", JOURNAL OF MATERIALS SCIENCE, Vol. 25, 1990

[0023] 6. J. G. Duh, et al., "High temperature oxidation of Fe-31Mn-9Al-xCr-0.87C alloys (x=0, 3 and 6)", JOURNAL OF MATERIALS SCIENCE, Vol. 25, 1990

[0024] 7. M. S. thesis "Phase Transformations in an Fe-8.8Al-30.0Mn-6.0Cr-1.0C Alloy", National Chiao Tung University, 1990, supervised by Prof. Liu Tzeng-feng (one of the inventors of the present invention)

[0025] From those discussed above, it is known: via appropriate composition design, the Fe—Mn—Al—C alloy, which has low density, high strength, and high toughness, is a material pretty fitting for golf-club heads; therefore, the patent Fe—Mn—Al—C alloys of different compositions have been tried to apply to golf-club heads. In order to demonstrate the difference among them, the published US and Taiwan patents relating to the applications of the Fe—Mn—Al—C alloys to golf-club heads are to be described below.

[0026] According to the Taiwan patent of Publication No. 178648 "Fabrication Method of the Precision Castings of a Fe—Mn—Al Alloy", the claim 1 thereof claims a Fe—Mn—Al alloy consisting of 22~36 wt. % Mn, 6~8 wt. % Al, 1.5~2.0 wt. % C, 1.0~1.5 wt. % Mo, and the balance of Fe, which has to use a solid-solution heat treatment at 1030~1050° C. for 1~2 hours and an aging heat treatment at 450~550° C. for 1~2 hours to obtain required toughness and strength.

[0027] According to the Taiwan patent of Publication No. 185568 "Fabrication Method of the Precision Castings of a Corrosion-Resistant Alloy", the claim 1 thereof claims a fabrication method of the precision castings of a corrosion-resistant alloy, wherein the casting of an alloy, which consists of 26~28 wt. % Mn, 6.5~8 wt. % Al, 5.0~6.0 wt. % Cr,

0.9~1.1 wt. % C, 0.2~1.5 wt. % Si, 1.0~1.2 wt. % Mo, 0.9~1.1 wt. % Cu, 0.02~0.04 wt. % Nb and the balance of Fe, requires a homogenization heat treatment at an atmosphere furnace, an atmosphere-controlled furnace, or a vacuum furnace.

[0028] According to the US patent of Publication No. 20030077479 "Low Density and High Ductility Alloy Steel for a Golf Club Head" (equivalent to the Taiwan patent of Publication No. 460591), the claim 1 thereof claims a low-density high-ductility iron-based alloy for golf-club iron heads consisting of 25~31 wt. % Mn, 6.3~7.8 wt. % Al, 5.5~9.0 wt. % Cr, 0.65~0.85 wt. % C, and the balance of Fe, which is hot forged at the temperature of 800~1050° C. The claim 2 thereof claims the alloy according to claim 1 but further comprising: 0.8~1.5 wt. % Si and 2.0~5 wt. % Ti. The claim 3 thereof claims the alloy according to claim 1 but further comprise: 0.5~1 wt. % Mo. Furthermore, in the patent specification thereof, the abstract, the summary of the invention, and the Remarks in FIG. 8 also mention that the alloy of this patent has to utilize a hot forging at the temperature of 800~1050° C. and a heat treatment at the temperature of 980~1080° C. for 1~24 hours to obtain a superior combination of ductility and tensile strength.

[0029] According to the US patent of Publication No. 20030082067 "Low-Density Iron Based Alloy for a Golf Club Head" (equivalent to the Taiwan patent of Publication No. 506845), the claim 1 thereof claims a low-density iron-based material for golf-club heads consisting of 28.0~31.5 wt. % Mn, 7.8~10.0 wt. % Al, 0.9~1.10 wt. % C, 0.35~2.5 wt. % Ti, and the balance of Fe, which is hot forged at the temperature of 900~1100° C. The claim 2 thereof claims the alloy according to claim 1 but further includes: 5.0~7.0 wt. % Cr. The claim 3 thereof claims the alloy according to claim 1 but further includes: 0.8~1.5 wt. % Si. Furthermore, in the patent specification thereof, the abstract, the summary of the invention, and the Remarks in FIG. 6 also mention: after the alloy of this patent is heat-treated at the temperature of 950~1270° C. for 1~24 hours, it can obtain a microstructure which consists of an austenitic matrix and varying ratios of precipitated phase (Ti, Fe)C_x, and a density lower than 6.6 g/cm³.

[0030] According to the US patent of Publication No. 20050006007 "Low Density Iron Based Alloy for a Golf Club Head" (equivalent to the Taiwan patent of Publication No. 584568), the claim 1 thereof claims a low-density iron-based alloy for golf-club heads consisting of 25~31 wt. % Mn, 7~10 wt. % Al, 5~7 wt. % Cr, 0.9~1.1 wt. % C, and the balance of Fe. The claim 2 thereof claims the alloy according to claim 1 but further includes: 0.8~1.5 wt. % Si. The claim 3 thereof claims the alloy according to claim 1 but further includes: 2~5 wt. % Cr. The claim 4 thereof claims the alloy according to claim 1 but further includes: 0.5~1.0 wt. % Mo. The claim 5 thereof claims the low density iron based alloy as claimed in claim 1 is hot forged at 800 to 1050° C. and has a surface roughness of 2.4 to 3 μm. Furthermore, in the patent specification thereof, the Chinese abstract, the summary of the invention, and the Notes of FIG. 6 in Detailed description of the invention also mention: the casting or the alloy having been plastically worked (hot worked or cold worked) are heat-treated at the temperature of 950~1270° C. for 1~24 hours to obtain a density lower than 6.6 g/cm³ and a microstructure with different ratios of precipitated phase; the alloy may also be hot forged at the

temperature of 800–1050° C. to obtain a superior surface property; the alloy may also be heat-treated at the temperature of 980–1080° C. for 1–4 hours and then heat-treated at the temperature of 500–650° C. for 4–8 hours, and the heat-treated alloy is cold rolled to modify the structure of the crystalline grains and then aging-treated to obtain a superior combination of tensile strength and ductility to meet the requirement of the golf-club head—low density, high strength and high corrosion resistance.

Fe—Mn—Al—C alloys have high carbon contents, the golf-club heads made from those Fe—Mn—Al—C alloys must be heat-treated in a vacuum furnace to prevent serious decarburization; the forging molds, This leads to a great increase in the fabrication cost of golf-club head.

[0033] Table shows the comparison of the disclosed Fe—Mn—Al-based alloys in the prior arts, with respect to the compositions and the heat treatment/forging conditions thereof as following:

| Application Pub. No. | Composition | | | | | | | | Forging and Heat-treatment Conditions |
|------------------------------|-------------|---------|---------|-------|-----------|----------|----------|----------------------------|--|
| | Fe | Mn | Al | Cr | C | Si | Mo | others | |
| TW 178648 | Bal. | 22~36 | 6~8 | | 1.5~2.0 | | 1.0~1.5 | | solid solution at 1030~1050° C. for 1~2 hrs and aging at 400~550° C. for 1~2 hrs |
| TW 185568 | 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 | Cu homogenization heat treatment |
| U.S. Pat. No. 20030077479 | Bal. | 25~31 | 6.3~7.8 | 5.5~9 | 0.65~0.85 | *0.8~1.5 | | *2~5 Ti | hot forging at 850~1050° C. and heat treatment at 980~1080° C. for 1~24 hrs |
| U.S. Pat. No. 20030082067 | Bal. | 28~31.5 | 7.8~10 | *5~7 | 0.9~1.1 | *0.8~1.5 | | *0.35~2.5 Ti | hot forging at 900~1100° C. and heat treatment at 950~1270° C. for 1~24 hrs |
| U.S. Pat. No. 20050006007 | Bal. | 25~31 | 7~10 | 5~7 | 0.9~1.1 | *0.8~1.5 | *0.5~1.0 | | hot forging at 850~1050° C. and then solid solution at 980~1080° C. for 1~4 hrs and aging at 500~650° C. for 4~8 hrs |
| TW 1235677 | 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 | solid solution at 1030~1080° C. for 15~60 mins and aging at 450~850° C. for 4~24 hrs |

*means content of element optionally added in this alloy

[0031] According to the Taiwan patent of Publication No. 1235677 “Low Density and High Ductility Iron Based Alloy for a Golf-Club Head”, the claim 1 thereof claims a low-density high-ductility iron-based alloy for golf-club heads consisting of 23.0~30.0 wt. % Mn, 6.3~10.0 wt. % Al, 5.0~9.0 wt. % Cr, 0.8~1.05 wt. % C, 0.2~10.0 wt. % Co and the balance of Fe, and the alloy is hot forged at the temperature of 1000~1050° C. to promote surface property so that the surface roughness will be below 3 μm. The claim 2 thereof claims the alloy according to claim 1 but further includes: 0.6~1.0 wt. % Si and 0.2~0.4 wt. % N. Furthermore, in the patent specification thereof, the Chinese abstract, the summary of the invention, the detailed description of the invention also mention: the casting of the Co-containing alloy of the invention is hot forged at the temperature of 1000~1050° C. and then heat-treated at the temperature of 1030~1080° C. for 15~60 minutes and then heat-treated at the temperature of 450~850° C. for 4~24 hours to obtain low density, high strength, high ductility, high corrosion resistance, and superior surface property and meet the requirement of the golf-club head.

[0032] Refer to Table to survey the abovementioned US and Taiwan patents regarding the application of the Fe—Mn—Al—C alloys to golf-club heads, it is found: the published patents of the Fe—Mn—Al—C alloys have to utilize a high-temperature long-time solution heat treatment and an aging heat treatment, or a hot-forging/rolling for grain-refining plus a long-time solution heat treatment and an aging heat treatment to obtain the strength and ductility required by golf-club heads. Further, as all the conventional

[0034] In the phase diagram of the Fe—Mn—Al—C alloy, there is a wide temperature range in the solid-liquid mixing region, i.e. a mush zone, wherein liquid-state metal and solid-state metal coexists. As the coexisting liquid-state metal and solid-state metal are very glutinous, the fluidity of the liquid alloy is poor, and the tiny letters of the logo, the minute U/V-section trenches of the striking face, and the thin-thickness region of the golf-club head are hard to form in the casting process but are mechanically carved otherwise; therefore, the fabrication time and cost of the golf-club head increases greatly, and the appearance design thereof is also limited by the poor castability in the thin-thickness region. Further, owing to the poor fluidity of the liquid alloy, the interdendrite porosity caused by the physical shrinkage during solidification cannot be fed, which results in the internal shrinkage porosity of the golf-club head and then the deformation or fracture of the striking face may be occurred when the golfer is hitting golf balls. Furthermore, the shrinkage porosity will be originators of fractures when the golf-club head is bent to adjust the loft angle between the head and the shaft or when the casting is forged.

[0035] Accordingly, the present invention proposes a low-density high-toughness alloy and the fabrication method thereof, which is adaptable to be a golf-club head material and can save the time and cost of fabricating the Fe—Mn—Al—C golf-club heads, to overcome the abovementioned problems.

SUMMARY OF THE INVENTION

[0036] One of objectives of the present invention is to provide a low-density high-toughness alloy and the fabrication method thereof, wherein the alloy of the present invention can obtain superior elongation, strength, damping capacity, and corrosion resistance without any heat treatment, hot working, or plastic cold working.

[0037] Another one of objectives of the present invention is to provide a low-density high-toughness alloy and the fabrication method thereof, wherein the fluidity of the liquid alloy is improved, and the castability and the plastic workability of the alloy, such as forgeability and ductility, are also promoted.

[0038] Yet another one of objectives of the present invention is to provide a low-density high-toughness alloy and the fabrication method thereof, wherein the fluidity of liquid alloy is improved, and the tiny letters, the trenches on the striking face, and thin-thickness regions of the golf-club head can be formed merely by only casting and without extra mechanical carving, and thereby, the fabrication cost and time thereof can be greatly saved.

[0039] Still another one of objectives of the present invention is to provide a low-density high-toughness alloy and the fabrication method thereof, wherein the fluidity of the liquid alloy is increased, and the interdendrite shrinkage porosity formed during the solidification process can be easily fed by the liquid alloy, which can solve the problem that the strength and ductility of the golf-club head is drastically lowered owing to the internal shrinkage porosity, and the problem that cracks are induced by the shrinkage porosity during the forging process or the rolling process; thereby, the yield thereof is greatly promoted.

[0040] Further another one of objectives of the present invention is to provide a low-density high-toughness alloy and the fabrication method thereof, wherein the alloy of the present invention not only has a density as low as 6.6–6.9 g/cm³, but also can even obtain a superior elongation as high as 30–60%, a superior tensile strength as high as 100–135 ksi, superior damping capacity, and superior corrosion resistance without any heat treatment, hot working, or plastic cold working in comparison with the conventional Fe–Mn–Al–C alloys.

[0041] The present invention proposes a low-density high-toughness alloy, comprising: equal to or greater than 23 wt. % but lower than or equal to 33 wt. % manganese, equal to or greater than 8.1 wt. % but lower than or equal to 9.8 wt. % aluminum, equal to or greater than 3 wt. % but lower than or equal to 7.8 wt. % chromium, equal to or greater than 0.6 wt. % but lower than or equal to 1.2 wt. % carbon, equal to or greater than 0.1 wt. % but lower than or equal to 0.5 wt. % silicon, and the balance of iron.

[0042] The present invention also proposes a fabrication method of a low-density high-toughness alloy, wherein a raw material, which comprises: equal to or greater than 23 wt. % but lower than or equal to 33 wt. % manganese, equal to or greater than 8.1 wt. % but lower than or equal to 9.8 wt. % aluminum, equal to or greater than 3 wt. % but lower than or equal to 7.8 wt. % chromium, equal to or greater than 0.6 wt. % but lower than or equal to 1.2 wt. % carbon, equal to or greater than 0.1 wt. % but lower than or equal to 0.5 wt. % silicon, and the balance of iron, is melted to form an alloy.

[0043] To enable the objectives, technical contents, characteristics and accomplishments of the present invention to be more easily understood, the theoretical basis of the alloy design and the embodiments of the present invention are to be described below in detail in cooperation with the attached drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0044] FIG. 1 is a diagram showing the relationship between the silicon content and the fluidity of the alloy consisting of 30.4 wt. % Mn, 8.8 wt. % Al, 5.1 wt. % Cr, 1.03 wt. % C, X wt. % Si, and the balance of Fe.

[0045] FIG. 2 is a diagram showing the relationship between the aluminum content and the fluidity of the alloy, consisting of 30.4 wt. % Mn, X wt. % Al, 5.1 wt. % Cr, 1.03 wt. % C, 0.18 wt. % Si, and the balance of Fe.

[0046] FIG. 3 is a diagram showing the depth profile of the alloying elements on the surface layer of the alloy containing: 30.4 wt. % Mn, 7.2 wt. % Al, 5.1 wt. % Cr, 1.03 wt. % C, 0.18 wt. % Si, and the balance of Fe.

[0047] FIG. 4 is a diagram showing the depth profile of the alloying elements on the surface layer of the alloy containing: 30.4 wt. % Mn, 8.1 wt. % Al, 5.1 wt. % Cr, 1.03 wt. % C, 0.18 wt. % Si, and the balance of Fe.

[0048] FIG. 5 is a diagram showing the potentiodynamic polarization curves performed in 5% NaCl solution for both the alloys containing different aluminum contents respectively consisting of 30.4 wt. % Mn, 7.2 wt. % Al, 5.1 wt. % Cr, 1.03 wt. % C, 0.18 wt. % Si and the balance of Fe, and 30.4 wt. % Mn, 8.1 wt. % Al, 5.1 wt. % Cr, 1.03 wt. % C, 0.18 wt. % Si and the balance of Fe.

DETAILED DESCRIPTION OF THE INVENTION

[0049] The alloy of the present invention is based on iron, manganese, aluminum, chromium, carbon, and silicon elements. According to the research of the inventors, when the Fe–Mn–Al–Cr–C alloy contains equal to or greater than 0.1 wt. % but lower than or equal to 0.24 wt. % silicon and equal to or greater than 8.1 wt. % but lower than or equal to 9.8 wt. % aluminum, a fine carbide (Fe, Mn)₃AlC_x (referred to as κ'-carbide hereinafter) having a L1₂ ordered phase will homogeneously and coherently precipitate within austenite matrix with FCC crystalline structure, and the casting thereof can obtain superior strength without any heat treatment. The atomic arrangement of the L1₂ ordered structure of the κ'-carbide is similar to that of the FCC structure of the austenite phase except that the types of atoms therein are not completely identical. The lattice constant of the κ'-carbide (a_κ'=0.376 nm) is very close to that of the austenitic matrix (a_γ'=0.371 nm), and there is only 1.3 wt. % difference between them. Therefore, a coherent interface can exist between the κ'-carbide and the austenitic matrix, and the atoms at both sides of the interface can be completely bonded together one by one separately just as the atoms inside their own phases; therefore, there is no edge dislocation to form on the interface because edge dislocations are to modify the huge stress field induced by different structures or different lattice constants. As the atoms at both sides of the interface can be completely bonded together one by one separately, the atoms on the interface between those

two phases are hard to move or diffuse. Therefore, when there is a coherent interface between the κ' -carbide and the austenite matrix, the fine κ' -carbides will not grow too rapidly inside the austenite matrix during cooling of the casting from pouring temperature, so that the casting will not change drastically from a ductile one to a brittle one. By comparison, the aforementioned patents have to use a high-temperature vacuum solid solution heat treatment and an aging heat treatment to obtain the microstructures of different ratios of precipitated phases before those alloys are used as the material of the golf-club heads. In contrast to those disclosed Fe—Mn—Al—C alloys, the alloy of the present invention may have fine κ' -carbides uniformly distributed in the austenite matrix and may also obtain a superior combination of elongation (30–60%) and tensile strength (100–135 ksi) even without any heat treatment.

[0050] Besides, in the present invention, equal to or greater than 0.1 wt. % or lower than or equal to 0.24 wt. % silicon is added into the Fe—Mn—Al—C alloy to improve its castability and promote its liquid-state fluidity. Therefore, the tiny logo letters of the casting, the minute U/V-section trenches on the striking face, and the thin-thickness regions of the golf-club head may be easily formed in the casting process without extra mechanical carving, and the fabrication cost thereof may also be saved. Owing to the promoted liquid-state fluidity, the molten alloy can effectively feed the interdendrite porosity caused by the physical shrinkage during the solidification process. Thus, the problems of cracks, which are induced by the internal shrinkage cavities during a plastic working process, such as a forging process and a rolling process, may be overcome. The inventors had undertaken a research to study the influence of the different silicon amount on the fluidity of the alloy comprising by weight percent: Fe-30.4% Mn-8.8% Al-5.1% Cr-1.03% C—X % Si; the 1550° C. molten silicon-free alloy and the 1550° C. molten alloys containing different ratios of silicon are poured into shell molds having spiral runner and pre-heated at 1000° C., and the lengths of the solidified alloys are compared with the length of the solidified silicon-free alloy, wherein X=0, 0.11, 0.17, 0.24, 0.30, 0.42, 0.60, 0.73, 0.85, and 1.17, and the length of the solidified silicon-free alloy is set to be 1. The test result is shown in FIG. 1. From FIG. 1, it can be seen that the silicon-free alloy has the shortest length and the relative lowest fluidity. When a slight amount of silicon as low as only 0.11 wt. % is added to the alloy, the length of the solidified alloy increases obviously. With the increase of silicon content, the length of the solidified alloy also increases proportionally until the silicon content reaches 0.42 wt. %; when the silicon content is above 0.42 wt. %, increasing the silicon ratio can no more increase the fluidity obviously.

[0051] When only the fluidity is considered, at least 0.42 wt. % silicon should be added into the alloy of Fe-30.4% Mn-8.8% Al-5.1% Cr-1.03% C. However, from the research performed by the inventors and implemented with SEM (scanning electronic microscope), EDS (energy dispersive spectrometer), TEM (transmission electronic microscope), and a tensile test, it can be seen: the as-cast structure of the alloy of Fe-30.4 wt. % Mn-8.8 wt. % Al-5.1 wt. % Cr-1.03 wt. % C with the addition of silicon of 0.3 wt. % or above contains dendrites and interdendrites interweaved among the dendrite structures. It is noted that during solidification process, the austenite dendrites solidify firstly, and meanwhile, the aluminum atoms and the silicon atoms are

expelled into the unsolidified interdendrite liquid phases; and with the decrease of temperature, the Al-rich and Si-rich liquid phases also solidify gradually. Although the Al and Si contents of the alloy of Fe-30.4 wt. % Mn-8.8 wt. % Al-5.1 wt. % Cr-1.03 wt. % C-0.3 wt. % Si are respectively only 8.8 wt. % and 0.3 wt. % on average, the Al and Si contents of the lastly solidified interdendrite regions are as high as 10.2 wt. % and 0.68 wt. % respectively, examined by SEM and EDX. From the TEM analysis and the phase identification, it is known: in the interdendrite regions, aluminum and silicon are the ferrite-forming elements, and in the Al-rich ferrite phase, increasing the silicon content will transform the disordered ferrite phase into a very brittle DO_3 ordered phase, which reduces the toughness of the alloy. It is also confirmed by the tensile test: when the silicon content in the alloy of Fe-30.4 wt. % Mn-8.8 wt. % Al-5.1 wt. % Cr-1.03 wt. % C-X wt. % Si is equal to or greater than 0.3 wt. %, the ductility of the as-cast alloy is reduced to 15% or below; such an alloy cannot be applied to the golf-club head unless it has been heat treated. When the silicon content of the alloy is equal to or greater than 0.3 wt. %, the ductility of the as-cast alloy without a heat treatment decreases obviously; however, as only 0.24 wt. % silicon is added to the alloy, the fluidity of the molten alloy could be significantly improved. Therefore, under the considerations of both ductility and fluidity, the silicon content of the alloy should be controlled to be equal to or greater than 0.1 wt. % but lower than or equal to 0.24 wt. %. In this case, the molten alloy can have a suitable fluidity, and the as-cast alloy without any heat treatment can also have a superior combination of toughness and strength. However, in the present invention, when the silicon content of the alloy is greater than 0.24 wt. % but lower than or equal to 0.5 wt. %, the alloy of the present invention can still possess fine elongation and strength via being heat treated for 1–3 hours at the temperature of 950–1200° C. The structures of present invention is distinct from those disclosed in Taiwan patent of Publication Numbers 178648, and US patents of Publication Numbers of 20030077479, 20030082067, and 20050006007, which have none silicon or have too great a silicon content as high as 0.8–1.5 wt. %.

[0052] The inventors had also undertaken a research to study the influence of the aluminum content on the fluidity of the alloy of Fe-30.4 wt. % Mn—X wt. % Al-5.1 wt. % Cr-1.03 wt. % C-0.18 wt. % Si; the 1550° C. molten alloys containing different ratios of aluminum are poured into shell molds having spiral runner and pre-heated at 1000° C., and the lengths of the solidified alloys are compared with the length of the solidified alloy containing 6.0 wt. % aluminum, wherein X=6.0, 7.4, 8.1, 9.1, 9.8, 10.6, and 11.8, and the length of the solidified alloy containing 6.0 wt. % aluminum is set to be 1. The test result is shown in FIG. 2. From FIG. 2, it can be seen: the alloy containing 6.0 wt. % aluminum has the shortest length and the lowest fluidity; with the increase of aluminum—a low-melting-point element, the fluidity of the alloy also increases.

[0053] As discussed above, the aluminum atoms will be segregated into the interdendrite regions during the solidification process, and the local aluminum content is much greater than the average aluminum content, which causes the reduction of toughness. From the observation performed by the inventors with TEM, aluminum is one of constituent elements of the carbide $(Fe, Mn)_3AlC_x$ (κ' -carbide); therefore, decreasing aluminum content will inhibit the κ' -car-

bide's precipitation on the austenite matrix and decrease the amount of κ' -carbide, which causes the reduction of strength. The inventors also utilized XPS/ESCA (X-Ray Photoelectron Spectroscopy/Electron Spectroscopy for Chemical Analysis) to analyze the oxides of the protective passivation layer on the surface of the alloy. From the analysis result, it is found that the passivation layer consists primarily of protective anti-corrosion Cr_2O_3 and Al_2O_3 , and minor proportion of protective anti-oxidation SiO_2 , and small proportion of non-corrosion-resistant oxides, such as $\text{FeO}(\text{Fe}_3\text{O}_4)$, Fe_2O_3 , $\text{MnO}(\text{Mn}_3\text{O}_4)$, and Mn_2O_3 . FIG. 3 and FIG. 4 are diagrams respectively showing the depth profiles of the surface oxides of the alloy of Fe-30.4 wt. % Mn-7.2 wt. % Al-5.1 wt. % Cr-1.03 wt. % C-0.18 wt. % Si and the alloy of Fe-30.4 wt. % Mn-8.1 wt. % Al-5.1 wt. % Cr-1.03 wt. % C-0.18 wt. % Si. From FIG. 3 and FIG. 4, the inventors make an important discovery: the content of Al_2O_3 , which can protect the metallic substrate, increases greatly when the aluminum content changes from 7.2 wt. % to 8.1 wt. % according to the atomic ratios of aluminum in FIG. 3 and FIG. 4 (The aluminum atoms in the surface layer exist in the form of Al_2O_3). FIG. 5 shows the potentiodynamic polarization curves performed in 5% NaCl solution for the alloy of Fe-30.4 wt. % Mn-7.2 wt. % Al-5.1 wt. % Cr-1.03 wt. % C-0.18 wt. % Si and the alloy of Fe-30.4 wt. % Mn-8.1 wt. % Al-5.1 wt. % Cr-1.03 wt. % C-0.18 wt. % Si. From FIG. 5, it is found that since the amount of the protective Al_2O_3 on the surface of the alloy with higher aluminum content of 8.1 wt. % increases greatly, the passivation current density (I_p) decreases obviously, and the passivation potential (ΔE) and the pitting-corrosion potential (E_{pp}) increase obviously; therefore, the corrosion resistance of the alloy of Fe-30.4 wt. % Mn-8.1 wt. % Al-5.1 wt. % Cr-1.03 wt. % C-0.18 wt. % Si containing 8.1 wt. % Al is much better than that of the alloy of Fe-30.4 wt. % Mn-7.2 wt. % Al-5.1 wt. % Cr-1.03 wt. % C-0.18 wt. % Si containing only 7.2 wt. % Al. Taking all the factors of the fluidity, elongation, strength, and corrosion resistance of the alloy into consideration and making a compromise between them, the aluminum content should be controlled to be equal to or greater than 8.1 wt. % but lower than or equal to 9.8 wt. %; in this case, the molten alloy of the present invention has superior fluidity, and the as-cast alloy of the present invention can also possess a superior combination of toughness and strength even without any heat treatment. The alloy of the present invention is distinct from those Taiwan patents of Publication Numbers 178648 and 185568, and US patent of Publication Number 20030077479, whose aluminum contents are lower than 8.0 wt. %.

[0054] Based on the abovementioned alloy design, which limits the silicon content to be equal to or greater than 0.1 wt. % but lower than or equal to 0.24 wt. %, and limits the aluminum content to be equal to or greater than 8.1 wt. % but lower than or equal to 9.8 wt. %, and to achieve the objective that the as-cast alloy can possess a superior combination of toughness and strength even without any heat treatment, the contents of the other alloying elements, such as Mn, Cr, C, are to be appropriately modified or limited as below.

[0055] Manganese is an austenite-stabilized element, which can increase the proportion of austenite and promote the elongation of the alloy. To enable the as-cast alloy to have a superior ductility, the manganese content has to be equal to or greater than 23 wt. %. However, when the manganese content is over 33 wt. %, the precipitation of

β -Mn phase will deteriorate the ductility of the alloy. Therefore, the manganese content should be controlled to be equal to or greater than 23 wt. % but lower than or equal to 33 wt. %. Carbon is not only an austenite-stabilizer but also a main constituent element of the carbide $(\text{Fe,Mn})_3\text{AlC}_x$ (κ' -carbide). Insufficient carbon content will decrease the proportion of austenite and inhibit the precipitation of κ' -carbide, which lead to the decrease of both ductility and strength of the alloy. Increasing the carbon content can increase the proportion of austenite and the amount of the κ' -carbide precipitated within the austenite matrix. However, excessive carbon content causes coarse carbides to precipitate on the grain boundary, which results in the decrease in the ductility of the alloy. Chromium is not only a ferrite-former element but also a carbide-forming element. Further, chromium can form a protective Cr_2O_3 oxide layer on the surface of the alloy and benefit the corrosion resistance of the alloy. Too low a chromium content will not provide enough protection from corrosion. Too high a chromium content with a high carbon content will cause the formation of Cr_7C_3 carbide with the HCP (hexagonal close packing) crystalline structure, which not only reduces the ductility of the alloy but also results in the chromium-depletion regions that will to be the attacked sites of pitting corrosion or intergranular corrosion. Therefore, to achieve the objective that the as-cast alloy can have a superior combination of toughness and strength even without any heat treatment, the chromium content should be limited to be equal to or greater than 3.0 wt. % but lower than or equal to 7.8 wt. %, and the carbon content should be restricted to be equal to or greater than 0.6 wt. % but lower than or equal to 1.2 wt. %. From the inventors' research, it is also found that adding molybdenum into the alloy can raise the pitting-corrosion potential (E_{pp}) of the potentiodynamic polarization curve performed in 5% NaCl solution and improve the pitting-corrosion resistance. Notwithstanding that there is a slight reduction in the ductility of the alloy, the strength of the alloy can be further raised when the addition amount of molybdenum does not exceed 1.5 wt. %. For the latest years, molybdenum has become very expensive; therefore, molybdenum will be selectively added into the alloy, and with surveying all the properties, whether molybdenum is added into the alloy depends on whether the Mo-free alloy can meet the requirement. Anyway, molybdenum may be flexibly added into the alloy within the range of at most 1.5 wt. % in order to get an optimal compromise between product quality and price competence.

[0056] In summary, the alloy of the present invention consists essentially of: 23~33 wt. % Mn, 8.1~9.8 wt. % Al, 3~7.8 wt. % Cr, 0.6~1.2 wt. % C, 0.1~0.24 wt. % Si and the balance of Fe, in which up to 1.5 wt. % Mo may also be added into the alloy of the present invention. The alloy of the present invention has superior fluidity in liquid state; even in non-heat-treated as-cast condition, the alloy of the present invention has a density as low as 6.6~6.9 g/cm³, a superior elongation as high as 30~60%, a superior tensile strength as high as 100~135 ksi, high damping capacity, and high corrosion resistance. When the Fe—Mn—Al golf-club heads are made from the alloy of the present invention, the fabrication cost can be reduced obviously.

[0057] The alloy of the present invention, which consists essentially of: 23~33 wt. % Mn, 8.1~9.8 wt. % Al, 3~7.8 wt. % Cr, 0.6~1.2 wt. % C, 0.1~0.24 wt. % Si, and the balance of Fe with up to 1.5 wt. % Mo being optionally added to the

alloy, can be melted in the atmosphere, in vacuum, or in a reducing atmosphere, and then cast into molds. Without any heat treatment, the casting can be directly sandblasted, ground, welded, drilled, surface-treated, and art-worked to form an as-cast type golf-club head. As the alloy of the present invention has superior ductility even in the as-cast state, the as-cast castings thereof are adaptable to the succeeding hot working or cold working and can be fabricated into forging type golf-club heads or complex type (casting plus forging) golf-club heads.

[0058] In order to prove the availability of the present invention, and to enable the persons skilled in the art to understand, make, and use the present invention, the embodiments of the present invention are to be described below; however, those embodiments are not intended to limit the scope of the present invention.

Embodiment 1

[0059] An alloy according to the present invention consists essentially of: 26 wt. % Mn, 8.3 wt. % Al, 6.0 wt. % Cr, 0.68 wt. % C, 0.18 wt. % Si, and the balance of Fe. The alloy may be melted with a high-frequency induction furnace, and then, the molten alloy is poured into pre-heated lost-waxed shell molds of golf-club heads. As the molten alloy has superior fluidity, it can easily fill into all the mold cavities and thin-thickness regions. After the castings together with the shell molds are cooled to room temperature, they are processed with the following steps of shell-mold shaking-out, cutting gates and runners, sandblasting, grinding, welding, drilling, surface-treatment, and art-working. Even without any heat treatment, the as-cast golf-club head can still possess superior properties and has a density as low as 6.74 g/cm³, an elongation as high as 59.1%, a tensile strength as great as 108.2 ksi, and superior corrosion resistance. Thus, the fabrication cost of golf-club heads can be greatly reduced.

Embodiment 2

[0060] An alloy according to the present invention consists essentially of: 30.4 wt. % Mn, 8.8 wt. % Al, 5.1 wt. % Cr, 1.03 wt. % C, 0.24 wt. % Si, and the balance of Fe. The alloy may be melted with a high-frequency induction furnace, and then, the molten alloy is poured into pre-heated lost-waxed shell molds of golf-club heads. As the molten alloy has superior fluidity, it can easily fill all the mold cavities and thin-thickness regions. After the castings together with the shell molds are cooled to room temperature, they are processed with the following steps of shell-mold shaking-out, cutting gates and runners, sandblasting, grinding, welding, drilling, surface-treatment, and art-working. Even without any heat treatment, the as-cast golf-club head can still have superior properties and has a density as low as 6.62/cm³, an elongation as high as 43.3%, a tensile strength as great as 124.5 ksi, and superior corrosion resistance. Thus, the fabrication cost of golf-club heads can be greatly reduced.

Embodiment 3

[0061] An alloy according to the present invention consists essentially of: 28 wt. % Mn, 8.8 wt. % Al, 5.1 wt. % Cr, 1.02 wt. % C, 0.21 wt. % Si, 1.0 wt. % Mo and the balance of Fe. The alloy may be melted with a high-frequency

induction furnace, and then, the molten alloy is poured into pre-heated lost-waxed shell molds for golf-club heads. As the molten alloy has superior fluidity, it can easily fill all the mold cavities and thin-thickness regions. After the castings together with the shell molds are cooled to room temperature, they are processed with the following steps of shell-mold shaking-out, cutting gates and runners, sandblasting, grinding, welding, drilling, surface-treatment, and art-working. Even without any heat treatment, the as-cast golf-club head can still possess superior properties and has a density as low as 6.83 g/cm³, an elongation as high as 35.2%, a tensile strength as great as 133.1 ksi, and superior corrosion resistance. Thus, the fabrication cost of the golf-club head can be greatly reduced.

[0062] In the present invention, the principles of alloy design and the knowledge of the microstructures in materials are applied to invent an alloy for golf-club heads, which has a density as low as 6.6–6.9 g/cm³ and a superior damping capacity, and can still have a superior elongation as high as 30–60%, a superior tensile strength as great as 100–135 ksi and a superior corrosion resistance even without any heat treatment, hot working, or plastic cold working. Via appropriate alloy design, the alloy of the present invention has improved fluidity and castability in liquid state, and has a superior plastic workability. Therefore, the present invention can greatly reduce the cost and save the time of the fabrication of the Fe—Mn—Al—C golf-club heads.

[0063] In conclusion, the composition of the alloy of the present invention is distinct from the compositions of the golf-club-head-related Fe—Mn—Al—C alloys disclosed in the US patents of Publication Numbers of 20030077479, 20030082067 and 20050006007, and the Taiwan Patents of Publication Numbers 178648, 185568 and I235677. The alloy of the present invention has a low density; further, even though none of heat treatment, cold working, and hot working (such as forging and rolling) is used, the as-cast alloy of the present invention can still have high toughness, high strength, high damping capacity, and high corrosion resistance. Furthermore, as the alloy of the present invention also has an improved fluidity in liquid state, the tiny letters, the trenches on the striking face, and the thin-thickness regions of the golf-club head can be formed completely in the casting process, and the mechanical carving is no more needed. The interdendrite can be easily fed by the molten alloy; thereby, the problem of internal shrinkage porosity is overcome, and the defective fraction and the fabrication cost of the Fe—Mn—Al—C golf-club heads are greatly reduced.

[0064] Those embodiments described above are to clarify the present invention to enable the persons skilled in the art to understand and use the present invention; however, the embodiments are not intended to limit the scope of the present invention; therefore, any equivalent modification and variation according to the spirit of the present invention is still to be included within the scope of the claims of the present invention stated below.

What is claimed is:

1. A low-density high-toughness alloy, comprising: equal to or greater than 23 wt. % but lower than or equal to 33 wt. % manganese, equal to or greater than 8.1 wt. % but lower than or equal to 9.8 wt. % aluminum, equal to or greater than 3 wt. % but lower than or equal to 7.8 wt. % chromium, equal to or greater than 0.6 wt. % but lower than or equal to

1.2 wt. % carbon, equal to or greater than 0.1 wt. % but lower than or equal to 0.5 wt. % silicon, and the balance of iron.

2. The low-density high-toughness alloy according to claim 1, further comprising up to 1.5 wt. % molybdenum.

3. The low-density high-toughness alloy according to claim 1, wherein the silicon content is equal to or greater than 0.1 wt. % but lower than or equal to 0.24 wt. %.

4. The low-density high-toughness alloy according to claim 2, wherein the silicon content is equal to or greater than 0.1 wt. % but lower than or equal to 0.24 wt. %.

5. The low-density high-toughness alloy according to claim 1, wherein the silicon content is equal to or greater than 0.24 wt. % but lower than or equal to 0.5 wt. %.

6. The low-density high-toughness alloy according to claim 2, wherein the silicon content is equal to or greater than 0.24 wt. % but lower than or equal to 0.5 wt. %.

7. The low-density high-toughness alloy according to claim 1, having a density ranging from 6.6 to 6.9 g/cm³, an elongation ranging from 30 to 60%, and a tensile strength ranging from 100 to 135 ksi.

8. A fabrication method of a low-density high-toughness alloy, comprising melting a raw material, which comprises: equal to or greater than 23 wt. % but lower than or equal to 33 wt. % manganese, equal to or greater than 8.1 wt. % but lower than or equal to 9.8 wt. % aluminum, equal to or greater than 3 wt. % but lower than or equal to 7.8 wt. % chromium, equal to or greater than 0.6 wt. % but lower than or equal to 1.2 wt. % carbon, equal to or greater than 0.1 wt. % but lower than or equal to 0.5 wt. % silicon, and the balance of iron, to form an alloy.

9. The fabrication method of a low-density high-toughness alloy according to claim 8, wherein said raw material further comprises up to 1.5 wt. % molybdenum.

10. The fabrication method of a low-density high-toughness alloy according to claim 8, wherein the silicon content

in said raw material is preferred to be equal to or greater than 0.1 wt. % but lower than or equal to 0.24 wt. %.

11. The fabrication method of a low-density high-toughness alloy according to claim 9, wherein the silicon content in said raw material is preferred to be equal to or greater than 0.1 wt. % but lower than or equal to 0.24 wt. %.

12. The fabrication method of a low-density high-toughness alloy according to claim 8, wherein the silicon content in said raw material is preferred to be equal to or greater than 0.24 wt. % but lower than or equal to 0.5 wt. %.

13. The fabrication method of a low-density high-toughness alloy according to claim 9, wherein the silicon content in said raw material is preferred to be equal to or greater than 0.24 wt. % but lower than or equal to 0.5 wt. %.

14. The fabrication method of a low-density high-toughness alloy according to claim 12, further comprising a step of heat-treating said alloy at the temperature ranging from 950 to 1200° C. for the duration ranging from 1 to 3 hours.

15. The fabrication method of a low-density high-toughness alloy according to claim 13, further comprising a step of heat-treating said alloy at the temperature ranging from 950 to 1200° C. for the duration ranging from 1 to 3 hours.

16. The fabrication method of a low-density high-toughness alloy according to claim 8, wherein said raw material is melted at the atmosphere, at vacuum, or at a reducing atmosphere.

17. The fabrication method of a low-density high-toughness alloy according to claim 8, wherein said alloy has a density ranging from 6.6 to 6.9 g/cm³, an elongation ranging from 30 to 60%, and a tensile strength ranging from 100 to 135 ksi.

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