Hydrogen capacity of the Fe-Ti-Al alloy prepared by high energy ball milling

Hadi Suwarno[1], S. Wiryolukito[2] and M.D.K. Dewa[2]

[1]Center for Nuclear Fuel Technology, National Nuclear Energy Agency, Gedung 20, Kawasan Puspiptek-Serpong, Tangerang Selatan 15314, Banten, Indonesia

[2]Laboratory of Material Science, Department of Mechanical Engineering and Aerospace, Bandung Institute of Technology, Jl. Ganesha 10, Bandung 40132, Indonesia *e-mail*: hadis@batan.go.id

Abstrak

Hidrogen memiliki nilai kalor tertinggi dari semua unsur kimia, regeneratif dan ramah lingkungan. Untuk aplikasi secara *mobile* dan stasioner kepadatan volumetrik dan gravimetrik hidrogen dalam bahan penyimpanan menjadi sangat penting. Paduan Fe-Ti sebagai penyimpan hidrogen telah diterapkan di berbagai bidang karena mampu menyerap hidrogen pada suhu kamar. Sayangnya, kapasitas menyimpan hidrogen sangat rendah. Sintesis dan karakterisasi paduan Ti-Fe-Al dengan perbandingan atom Fe: Ti: Al = 10: 10: 1 dibuat dengan teknik pemaduan mekanik dalam larutan toluena dan sifat penyerapan hidrogen dari sintetik yang dihasilkan telah dilakukan. Serbuk Fe-Ti-Al digiling bersama-sama dengan waktu milling 30 jam di dalam mesin *ball mill* energi tinggi. Spesimen yang digiling dianalisis dengan difraktometer sinar-X. Analisis kualitatif dan kuantitatif dihitung dengan metode *Rietveld* yang dikembangkan oleh Fuji Izumi. Analisis pola difraksi sinar-x hasil giling paduan Fe-Ti-Al menunjukkan hanya ada senyawa FeTi bisa diamati dan tidak ada senyawa Fe-Al atau Ti-Al. Hasil hidriding pada suhu kamar menunjukkan bahwa paduan Fe-Ti-Al berubah menjadi $FeTiH_2$ dan TiH_2. Kapasitas serapan hidrogen yang tinggi dan suhu hidridisasi rendah dari paduan Fe-Ti-Al dibandingkan dengan Fe-Ti paduan memungkinkan paduan ini dapat dipromosikan sebagai bahan penyimpanan hidrogen yang baru.

Kata kunci: Sistem Fe-Ti, metal hidrid, simpan hidrogen, *ball mill* energy tinggi

Abstract

Hydrogen exhibits the highest heating value of all chemical fuels, regenerative and environment friendly. For mobile and stationary applications the volumetric and gravimetric density of hydrogen in a storage material is crucial. Fe-Ti alloys for storing hydrogen have been applied in many areas because it absorbs hydrogen at room temperature. Unfortunately, its capacity of storing hydrogen is very low. The synthesis and characterizations of Ti-Fe-Al alloy with the atomic ratio of Fe:Ti:Al = 10:10:1 prepared by mechanical alloying technique in toluene solution and the hydrogen absorption properties of the synthetic yielded have been performed. Fe-Ti-Al elemental powders were milled together with the milling time of 30 h, in a high energy ball mill. The milled specimens are analyzed with an X-ray diffractometer. Qualitative and quantitative analysis were calculated using *Rietveld method* developed by Fuji Izumi. The refinement analysis of the x-ray diffractions results for Fe-Ti-Al alloy, only FeTi compound was observed and no Fe-Al or Ti-Al compounds. On hydriding at room temperature, the milled Fe-Ti-Al was transformed into $FeTiH_2$ and TiH_2. Consider the high hydrogen capacity and the low hydriding temperature of the Fe-Ti-Al alloys compared to that of Fe-Ti alloy, it could be promoted as new hydrogen storage materials.

Keywords: Fe-Ti systems, metal hydride, hydrogen storage, high energy ball milling

1. Introduction

Hydrogen can be classified as a renewable fuel produced directly from solar light or indirectly via electricity from a renewable source e.g. wind and hydro power, or nuclear power. Some of the earliest work in solar thermo chemistry was dedicated to the direct thermal dissociation of water, also known as thermolysis of water, i.e. $H_2O \rightarrow H_2 + \frac{1}{2} O_2$. However, until today, almost all hydrogen is made from natural gas by a process called

steam reforming. Steam reforming does not reduce the use of fossil fuels but rather shifts them from end use to an earlier production step, giving rise to large quantities of carbon dioxide emissions to the atmosphere [1]. Using nuclear as the primary energy source for hydrogen production is advantageous for two main reasons. Firstly, nuclear reactors do not emit any greenhouse gases (GHG), the most important being CO_2. Secondly, nuclear energy can contribute to large-scale hydrogen production. A new method called the iodine-sulfur process is currently under development for hydrogen generation. The gaseous products resulting from the water thermolysis need to be separated at high-temperatures to avoid recombination that may form an explosive mixture [2,3].

Utilization of hydrogen as transportation fuel requires storage media. There are three different options to store hydrogen: liquefied hydrogen, compressed hydrogen gas, and solid hydrogen storage with their specific advantages and disadvantage. Storing hydrogen in the form of liquid needs certain operating conditions, i.e. a temperature of 21.2 K at ambient pressure. Due to the low critical temperature of hydrogen liquid (33K), hydrogen can only be stored in open systems, because no liquid phase exists above the critical temperature and the pressure in a closed storage system at room temperature could rise to about 10^4 bars. Though liquid hydrogen has a higher volumetric hydrogen density (70.8 kg.m^{-3}) and gravimetric density, compared to the other techniques, this storing method requires a large amount of energy to liquefy the hydrogen gas, and a special vessel with an effective heat insulation layer to reduce evaporation of the liquid hydrogen over a long period [4]. Storing hydrogen as gas is the most common storage system with a maximum pressure of ca. 200 bars. New light weight composite cylinders have been developed which are able to withstand a pressure up to 800 bar so the hydrogen can reach a volumetric density of 36 kg·m^{-3}, approximately half as much as that in the liquid form at the normal boiling point.

A number of storage methods are being developed, one of which involves storing hydrogen in the form of metal hydrides. Metal hydrides are applied for reversible solid-state hydrogen storage at low pressures with high volumetric capacity for homes, business, and on board transport vehicles purposes [5]. Storing hydrogen as chemical or physical combinations with materials in the form of metal hydrides, complex hydrides and carbon materials, or produced on-board the vehicle by reforming methanol, etc. posses attractive attributes for hydrogen storage [6]. This study focuses on storing hydrogen in the form of metallic hydrides, i.e. metal and intermetallic compounds which together with hydrogen metallic hydrides. As known, many transition metals and their alloys react with hydrogen at elevated temperature to form hydrides, including magnesium-nickel, magnesium copper and iron titanium.

Iron alloyed with titanium has been used for years to store hydrogen in the solid form. FeTi system has been examined at various times due to its moderate kinetics with relatively high equilibrium hydrogen pressure (~ 4.5 atm) at room temperature. However, low storage capacity (1.8~1.9 wt%) and O_2, H_2O, CO poisoning problems could not be resolved fully for practical applications. FeTi has CsCl-type structure which corresponds to $Pm\bar{3}m$ space group with a lattice parameter of 2.9789Å [7].

FeTi reacts readily to form FeTiH$_{\sim1}$ (β-phase) and FeTiH$_{\sim2}$ (γ-phase) with tetragonal and cubic structures (Reilly and Wishwall, 1974), orthorombic and monoclinic structures (Thompson, et al., 1978 and 1979), and orthorombic structure with difference cel parameters (Fisher et al., 1978 and 1987). The formation energies of FeTiH$_x$ *(x =1-6)* hydrides has been systematically investigated by Kinachi [8] on the basis of crystal and electronic structures and structural stability using Fritz-Haber-Institute GGA pseudopotential (Fuch and Scheffler, 1999) to represent the atomic cores. The results were in agreement with the experimentally determined ground states for FeTiH and FeTiH$_2$. Synthesis of the FeTi single phase alloy with

CsCI-tpe structure has been conducted by Hotta et al. [7]. It was found that by mixing Ti (< 100 µm) and Fe (< 100 µm) in a high energy ball milling for 20 hours single phase FeTi alloy could be obtained with a crystallite size of around 4.5 – 6.0 nm. Ball-milling involves heavy deformation of the powders so the material as prepared is far from equilibrium and contains a high concentration of strain and defects. Under such condition, hydrogen absorption of the powders will not occur and therefore activation process is required. A typical activation of polycrystalline FeTi which consists of annealing at 450 ^{o}C under hydrogen at high pressure should be conducted (L. Zaluska et. al., 1995).

Magnesium and its derived alloys are looked upon as promising candidates of hydrogen storage due to their high theoretical storage capacity (7.6 wt%), light weight and low cost. However, high operating temperatures and slow kinetics prevent them from practical application (L. Zaluska et. al., 1999). In practice both absorption and desorption of hydrogen require a temperature of at least 350–400 ^{o}C and even then only occur over a time scale of hours. Alloying magnesium with other metals (Ni, Al, Ti, Fe) reduced the hydrogen absorption-desorption temperature into about 300 ^{o}C. Unfortunately, the hydrogen capacity of the alloy is also decreased significantly. Intermetallic Mg_2Ni absorbed hydrogen at a capacity of up to 3.6 wt% under hydriding temperature of 250 – 350 ^{o}C (L. Zaluska et. al., 1995). Mg-alloyed with Al will form stable Mg_2Al_3 and $Mg_{17}Al_{12}$ compounds [9,10,11]. The two compounds can be obtained by milling or melting of the elemental constituent at a stoichiometry compositions. The hydriding results showed that the Mg-Al alloys absorbed hydrogen at varied capacity of 4.0 – 4.5 wt% at a temperature of 300 – 350 ^{o}C. Mg-alloyed with Ti has been investigated by several researchers. Kyoi [12] studied mixing of MgH_2 with $TiH_{1.9}$ at 8 GPa and 600 ^{o}C and found that new

hydride in the form of Mg_7TiH_x can be formed with a maximum hydrogen capacity of 5.5 wt%. On decomposition, the alloy forms Mg and $TiH_{1.9}$ at 332 ^{o}C by releasing about 4.7 wt % of hydrogen. Suwarno [13] prepared the Mg_2Ti alloy by a SPEX 8000 high energy ball milling and reported that Mg_2Ti compound can be obtained after 30 h of milling. On hydriding at 300 ^{o}C the alloy absorbs hydrogen up to 6 wt%. Sohn and Emami [14] conducted quite a similar experiment as that of Kyoi, using MgH_2 and TiH_2 powder as the initial components. After milling for 12 h, the alloy was heated at 350 ^{o}C and on dehydriding the hydrogen desorbed was around 6 wt%. Again, Mg-Ti alloys still require high temperature operation. Mg-Fe alloys also have been researched for years. Herrich, et al. [15] reported that milling MgH_2 and Fe powders under a hydrogen pressure of 7 bar for 40 h could yield a Mg_2FeH_6 compound. Unfortunately, the presence of oxygen disturbs the formation of ternary compound. Suwarno [16] prepared the Mg-Fe alloy by a SPEX 8000 high energy ball milling and reported that no Mg-Fe compounds were observed after 70 h of milling and the ternary metal hydride of Mg_2FeH_6 compound can be formed from individual component on hydriding at 300 ^{o}C.

Retuerto [17] prepared Mg_2FeH_6 compound by mixing the MgH_2 and Fe powders. The reaction took place in a piston-cylinder press, at moderate reaction pressures (2 GPa), and temperatures in the 750-850 ^{o}C range, for short reactions times of less than 1 h. Again, Mg-Fe alloys necessitate high temperature operation.

In this paper, investigation of the hydrogen capacity of the Fe-Ti-Al with the atomic ratio of Fe:Ti:Al = 10:10:1 alloy prepared by a high energy ball milling is performed in order to find new compound that can store hydrogen at a higher capacity at room temperature, making it suitable for practical applications. The composition of the alloy is selected according to the enthalpy calculation where the alloy

prepared should have ΔH < -48 kJ/gmole. To be presented also here the hydrogen capacity of Fe-Ti alloy obtained by other researchers and Fe-Ti-Mg alloy previously investigated by the Author.

2. Material and method

The starting material consists of elemental crystalline powders of titanium purchased from Aldrich at a purity of 99.7% metal basis with a particle size of -100 mesh, iron purchased from Aldrich at a purity of 97% with a particle size of -325 mesh, and aluminum purchased from Aldrich at a purity of 99% with a particle size of -200 mesh. About 15 grams of Fe, Ti, and Al elements with the atomic ratio of Fe:Ti:Al = 10:10:1, denoted as $Fe_{10}Ti_{10}Al$, are mixed together with stainless steel balls and then poured into a vial together with the toluene. The ball-to-specimen ratio is 8:1 and the milling is performed for 30 h at room temperature in the toluene solution. The vial is made of stainless steel with a diameter of 5.1 cm and 7.6 cm in length. The stainless steel balls have a diameter of 12 mm. The vial is then put into a high energy milling (HEM), Mixer Mill, type PW 700i, made by local company. One cycle of milling of a normal blending speed of 1400 rpm, run time of 90 minutes, and an off time of 30 minutes, means that 10 h of milling requires 5 cycles of operation.

Hydriding experiment is conducted in a Sievert system developed by the Author, a system consisting of a turbo molecular pump, a rotary vacuum pump, and several components for high vacuum purposes, which can be operated under high vacuum condition up to 1×10^{-5} mbar with a maximum operating pressure of 1000 mbar or under positive pressure with a maximum operating pressure of 60 bar. About 3-5 grams of Fe_2Ti milled powder are placed into the hydriding system and then annealed for 1 h at 430 ^{o}C for removing toluene from the powder and for recrystallization. After cooling down to room temperature the weight of Fe_2Ti powder is measured. To avoid direct contact of the powder with air during removal of the powder from the system for weighing purpose, ultra high purity argon is admitted to the system. Hydrogen absorbed in the specimen can be calculated from the pressure changes in the system during measurements using a formula developed by the Author as follow:

$$n_{abs}(P_{SC}^{eq}) = \frac{\Delta P_{RC} V_{RC}}{RT_{RC}} - \frac{\Delta P_{SC} V_{SC}}{RT_{SC}} \qquad (1)$$

where $n_{abs}(P_{SC}^{eq})$ is the number of hydrogen absorbed in the specimen under equilibrium state, ΔP_{RC} is reservoir pressure, V_{RC} is reservoir volume, ΔP_{SC} pressure in the specimen holder, V_{SC} is volume of specimen holder, R gas ideal constant, T_{RC} is reservoir temperature and T_{SC} is holder temperatur. The quality and quantity of the phases formed are analyzed using a Philip PW 1710 x-ray diffractometer (XRD), with Cu as the anode tube and λ = 1.5406 Å. Continuous scanning is conducted at 0.02° step size and 0.5 second/step. The scanning results are analyzed using Rietveld method developed by Fuji Izumi[18].

3. Result and discussions

Figure 1 shows the refinement XRD result of the $Fe_{10}Ti_{10}Al$ after milling for 30 h. It is showed that after milling the three components mainly form FeTi compound, about 75 wt% (see Table 1), while the rest can be identified as Fe (21.33 wt%) and Ti (3.66 wt%). Supposed that the milling time is extended, the maximum FeTi compound should be not exceded 90 wt%.
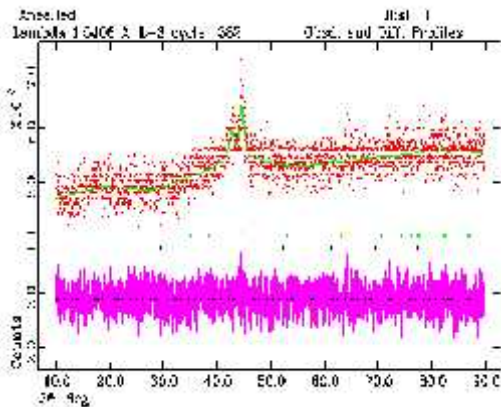
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Figure 1. The XRD refinement result for
Fe$_{10}$Ti$_{10}$Al after milling for 30 h.

Table 1. Mass fraction of Fe$_{10}$Ti$_{10}$Al specimen
after milling for 30 h.

No	Compound	Phase	Mass Fraction (wt.%)
1	Titanium	Ti	3.66
2	Iron	Fe	21.33
3	Iron Titanium	FeTi	75.01

Figure 2 shows the refinement XRD result of the Fe$_{10}$Ti$_{10}$Al after hydriding at room temperature. It is showed that on hydriding the FeTiAl compound absorbed hydrogen in the from of FeTiH at 55.35 wt%, TiH$_2$ at 24.03 wt%, and the rest is Fe at 20.62 wt%, as presented in Table 2. The presence of TiH$_2$ with the quantity of higher than its initial one is difficult to be explained. Referring to the enthalpy formation proposed by Anders Andreasen [19], the binary TiH$_2$ can be formed easily than the ternary FeTiH. Therefore, on hydriding parts of FeTi decomposes into Fe and Ti, where Ti will react with hydrogen to form TiH$_2$.

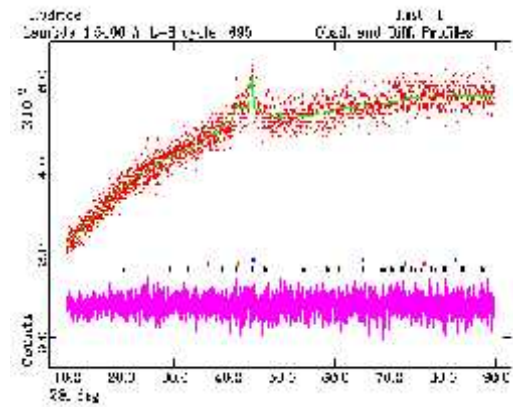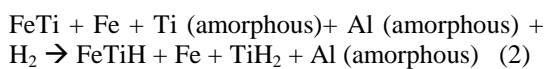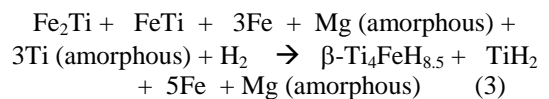The hydriding reaction of the Fe$_{10}$Ti$_{10}$Al specimen can be written as follows:

FeTi + Fe + Ti (amorphous)+ Al (amorphous) + H$_2$ $\rightarrow$ FeTiH + Fe + TiH$_2$ + Al (amorphous) (2)

Figure 2. The XRD refinement result for
Fe$_{10}$Ti$_{10}$Al after hydriding at room temperature.

Tabel 2. Mass fraction of Fe$_{10}$Ti$_{10}$Al alloy after hydriding.

No	Compound	Phase	Mass fraction (wt.%)
1	Titanium Hydride	TiH$_2$	24.03
2	Iron	Fe	20.62
3	Iron Titanium Hydride	FeTiH	55.35

Different from the Fe$_{10}$Ti$_{10}$Al alloy, the Mg$_2$Ti$_5$Fe$_6$ previously prepared be the Author exhibits that the formation of FeTi is disturbed by the formation of Fe$_2$Ti [20]. On hydriding at room temperature the Mg$_2$Ti$_5$Fe$_6$ alloy forms ternary β-Ti$_4$FeH$_{8.5}$ compound. The hydriding reaction of the Mg$_2$Ti$_5$Fe$_6$ specimens can be written as follows:

Fe$_2$Ti + FeTi + 3Fe + Mg (amorphous) + 3Ti (amorphous) + H$_2$ $\rightarrow$ β-Ti$_4$FeH$_{8.5}$ + TiH$_2$ + 5Fe + Mg (amorphous) (3)

Suppose the ꙅ-Ti$_4$FeH$_{8.5}$ compound consisted of FeTiH, 3TiH$_2$ and 1.5H$_2$, therefore the energy formation of ꙅ-Ti$_4$FeH$_{8.5}$ is little higher than FeTiH but much smaller than FeTiH$_2$. Consequently the presence of Mg increase the energy formation of Fe-Ti-hydrid, while none for the case of Al. Atomic composition of Fe:Ti = 1:1 is suggested to be the main factor in the formation of FeTi compound. Compared to the Mg$_2$Ti$_5$Fe$_6$ alloy above, where the major component after milling is still Fe phase and where the present

of Mg disturbs the formation of Fe-Ti compounds, the presence of Al do not disturb the formation of FeTi compound and consequently increase the hydrogen capacity in the Fe-Ti alloy. Similar to Mg, the disappearance of Al is due to the irregular shape in the alloy. Figure 3 shows the XRD refinement results for $Mg_2Ti_5Fe_6$ specimen before and after hydriding at room temperature.
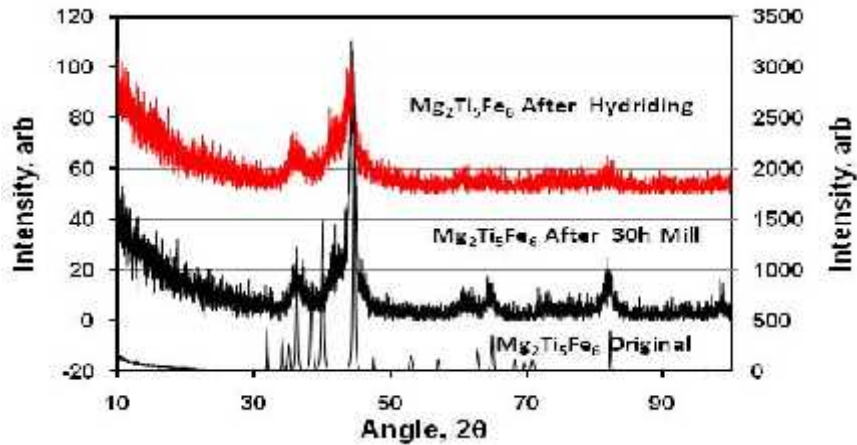

Figure 3. The XRD refinement result for $Mg_2Ti_5Fe_6$ alloy original (bottom), after milling for 40 h (middle), and after hydriding at room temperature (upper).

Figure 4 shows the hydriding results of $Fe_{10}Ti_{10}Al$ specimen, presented together with the FeTi obtained by Zaluska [21] and the Fe_2Ti and $Mg_2Fe_5Ti_6$ obtained by Suwarno [20]. It is exhibited that $Fe_{10}Ti_{10}Al$ specimens seems to absorb hydrogen higher than the other. It contains almost 2.5 at% hydrogen. Zaluska point out that the plateau pressure for Fe-Ti can be found at a pressure of about 1 bar, which comes from the equilibrium pressure of $FeTi + \frac{1}{2}H_2 <=> FeTiH$. It is suggested that the change in hydrogen absorption characteristics for the nanocrystalline Fe_2Ti (in the range of formation of $Fe+TiH_2$), due to the excess of Fe and the highly disordered structures, is caused by the influence of structural defects and internal strain on the metal-hydrogen phase diagram. It can be seen from the plateau pressure of $Mg_2Ti_5Fe_6$ and especially $Fe_{10}Ti_{10}Al$ alloys, in which it is much lower compared to that of Fe_2Ti and FeTi. The lower plateau pressures of both $Mg_2Ti_5Fe_6$ and especially $Fe_{10}Ti_{10}Al$ specimens compared to that of pure Fe-Ti alloys an indication that they absorbed hydrogen faster and higher than that of pure Fe-Ti alloys and therefore they can be promoted as candidates for hydrogen storage material.
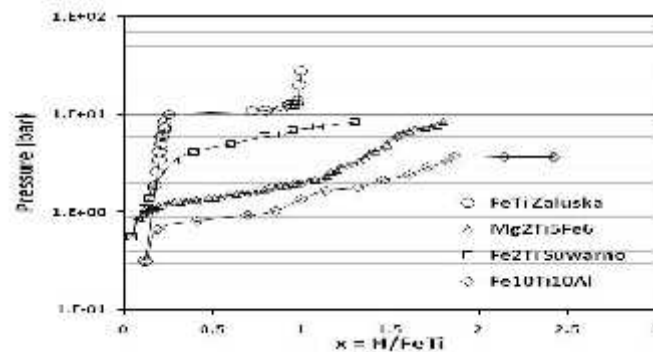

Figure 4. Hydrogen capacity of the $Mg_2Ti_5Fe_6$ and $Fe_{10}Ti_{10}Al$ specimens at room temperature, presented together with Fe-Ti alloys [7,8].

4. Conclusion

Synthesis of the $Fe_{10}Ti_{10}Al$ specimens can be conducted using a high energy ball milling. On milling, the $Fe_{10}Ti_{10}Al$ alloy is converted into FeTi compound as the major component while the rest is Fe. On hydriding the $Fe_{10}Ti_{10}Al$ specimen forms FeTiH compound as the major component. With regards to the thermal properties, where both of β-$Ti_4FeH_{8.5}$ and FeTiH have quite similar heat formation, continues investigation using a computer code is required to determine the precise composition of Fe:Ti:Al specimens.

Acknowledgment

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