東海大学大学院令和2年度博士論文

A Proposal for Synchronic Transportation of Water and Energy by Hydrogen Energy System Utilizing Hydrogen Storage Alloys

（水素貯蔵材料を用いた水素エネルギーシステムによる水とエネルギー共輸送の提案）

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Chapter I: INTRODUCTION

1.1. Research background

Along with the spread of activities on The Sustainable Development Goals (SDGs), the realization of a sustainable society is expanding worldwide. SDGs are the outline for achieving a better and more sustainable future for our planet. They handle the global challenges we face, including poverty, inequality, climate change, environmental deterioration, peace, and justice. The 17 Goals are all related, and in order to leave no one behind, we must achieve them all by 2030 [1].

It is necessary to realize the improvement of people's Quality of Life (QOL) as soon as possible in order to break away from the social system based on the massive consumption of fossil energy resources. In this study, we consider an example of Kazakhstan with related SDGs including Goal 6 – Ensure access to water and sanitation for all; Goal 7 – Ensure access to affordable, reliable, sustainable, and modern energy; Goal 13 – Take urgent action to combat climate change and its impacts [1].

Kazakhstan is a country located in the central part of the Eurasian continent and it is rich in coal, oil, and other mineral resources. Most cities have developed along the historical Silk Road. The existing social infrastructure was established under the Soviet Union in the 20th century and is still used today despite its aged condition.

In terms of the water supply system, each large city obtains water from the nearest river using aged facilities. However, the amount of incoming river water is reduced due to its utilization for neighboring countries' agriculture. Moreover, it arrives at the borders of Kazakhstan already polluted.

Not only industrial emissions and agricultural pesticides are causes of polluted tap water, but there is also nuclear pollution from nuclear tests during the Cold War in the north-eastern to middle-southern parts of the country.

Under these conditions, the drinking water supply issue is a significant problem, including how to supply drinking water from limited water resources to large urban areas. This proposal is unique and rarely considered in Japan, an island with plenty of clean water.

This study proposes hydrogen energy as an alternate, new, sustainable, affordable, and reliable energy, as well as a drinking water supply source by utilizing hydrogen energy using fuel cells. As a first feasibility study, we propose a simple hydrogen energy system model as a solution for the water supply issues in Kazakhstan by utilizing the existing infrastructure as much as possible while considering cost and implementation period. Moreover, this research focuses on the hydrogen storage and transportation method, which will be water transportation.

1.2. Kazakhstan: country profile

Kazakhstan is located in Central Asia, on both sides of the two continents, Asia (85%) and Europe (15%), or rather on Eurasia's center. The coordinates of the country are between 45 and 87 degrees east and between 40 and 55 degrees north.

The country is the 9th largest territory in the world, with an area of 2.724 million km^2. The total length of Kazakhstan's borders is over 15000 km, of which 12000 km is overland, and 3000 km of borders run through the Caspian and Aral seas. Kazakhstan shares a border with Russia to the north and the west (7591 km), with China to the east (1783 km), with Kyrgyzstan (1242 km), Uzbekistan (2351 km), and Turkmenistan (426 km) to the south. (Fig. 1) [2].

From the Caspian lowland to the Altai Mountains or west to east, the total distance is 3000 km. From the West Siberian Plain to the Kyzylkum Desert and the Tien Shan Mountains or north to south, the distance is 1700 km.

Fig. 1 Kazakhstan on a world map [2].

Kazakhstan gained independence from the Soviet Union on December 16, 1991. The Republic of Kazakhstan is a unitary state with the presidential system of government. According to Article-1 of the Constitution of the Republic of Kazakhstan, The Republic of Kazakhstan proclaims itself as a democratic, secular, legal and social state whose highest values are an individual, life, rights, and freedoms.

Since independence in 1991, the GDP (Gross Domestic Product) of the country has increased from US$ 26.93 billion (1991) to US$ 179.34 billion (2018) (Fig. 2) [3]. According to British experts, out of 25 of the most dynamic economies of the first decade of the 21st century, Kazakhstan is ranked third, just behind China and Qatar. According to the World Bank, the country has joined the group of countries with above-average income.

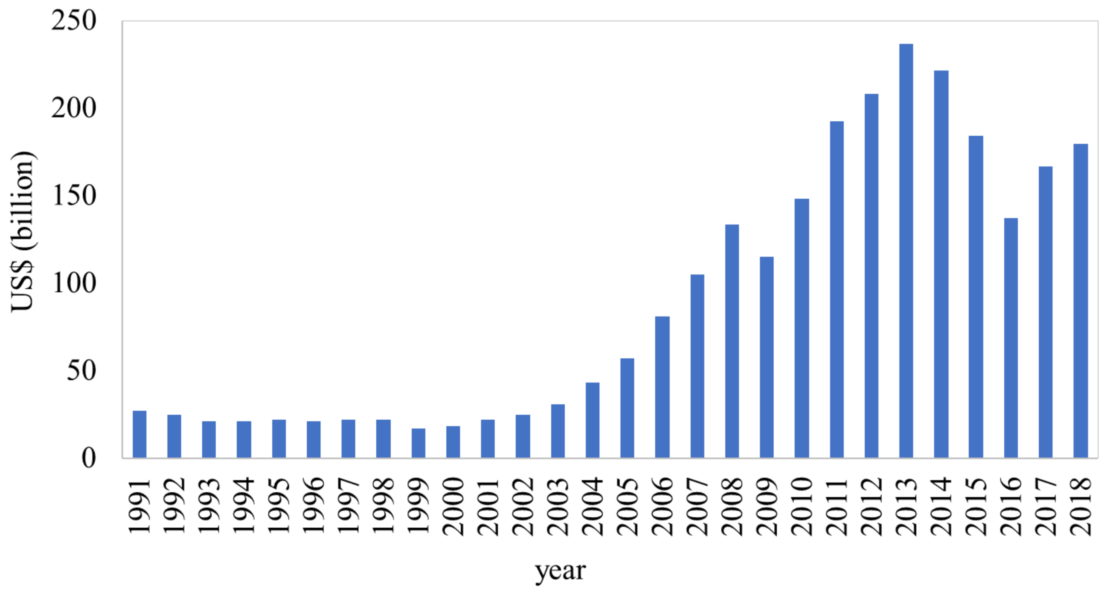

Fig. 2 GDP of Kazakhstan (1991-2018) [3]

Over the years of independence, Kazakhstan attracted US$ 200 billion of foreign investment, accounting for nearly 70% of the total volume of foreign investments in Central Asia. Major donor countries during 2012-2016 are summarized in Table 1. As we see, Japan made an immense contribution to the development of Kazakhstan.

Japan's aid record:

(1) Loan aid: Approximately US$ 951 million (cumulative up to FY2017)

(2) Grant aid: Approximately US$ 63.4 million (cumulative total up to FY2017)

(3) Technical cooperation: Approximately US$ 135 million (cumulative total up to FY2017)[4].

Table 1 ODA (Official Development Assistant) performance of DAC (Development Assistant Committee) countries (2012-2016) (based on expenditure, million US$) [4]

Year	1	2	3	4	5	Total
2012	Japan 30.89	USA 23.04	Germany 15.53	UK 5.22	France 3.28	85.61
2013	Japan 36.99	USA 29.70	Germany 14.91	France 4.08	UK 3.17	95.67
2014	USA 30.54	Germany 14.47	France 4.82	Japan 3.18	UK 3.11	61.73
2015	USA 18.70	Germany 13.72	UK 8.45	France 5.33	Austria 1.76	53.38
2016	USA 33.90	Germany 15.20	UK 4.73	France 4.18	Japan 2.96	68.30

Kazakhstan is currently implementing the "New Silk Way," a large-scale project that aims to revive its historical role as a connecting link in the continent. It will transform Kazakhstan into the most significant business and transit hub of the region, a bridge between Europe and Asia. This mega-project will almost double the volume of cargo traffic passing through the country by 2030.

The country is structured into 18 administrative zones and cities of national significance. Nur-Sultan (Astana) is the country's capital city, and Almaty is the largest city with a population of one million. The population of Kazakhstan exceeds 18 million people. The average population density is 7 persons/ km^2 (Fig. 3) [5].

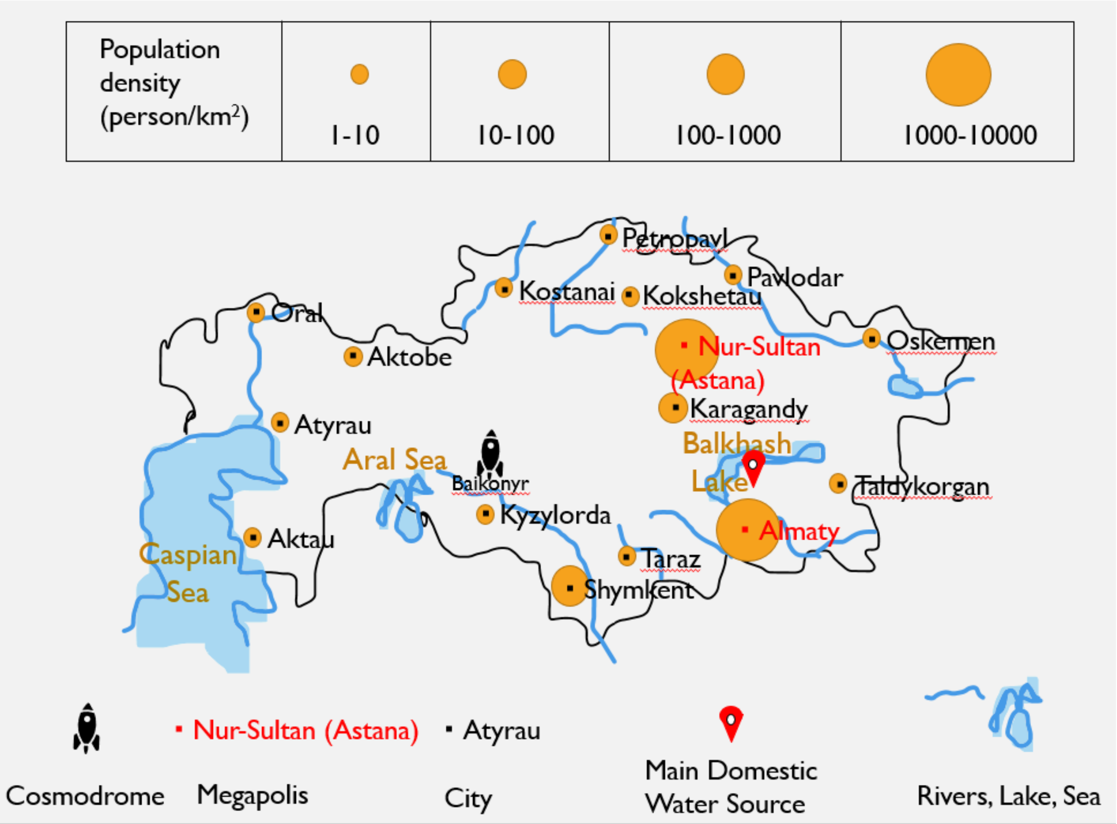

Fig. 3 Population density of Kazakhstan [5]

Kazakhstan is the largest landlocked country in the world. Most regions of the country are desert (44%) and semi-desert (14%). 26% of Kazakhstan's territory is steppe, and only 5.5% is forest. The country's remoteness to the world's oceans is the main reason for the country's continental climate with pervasive drought throughout the country. Summers are hot and dry, and winters are cold and snowy. The average temperature in January is around -19 °C, whereas the average temperature in July is around 19 °C. The lowest temperature is -59 °C, and the highest temperature is 49 °C [2].

1.3. Energy situation and environmental problems

Kazakhstan has abundant natural and mineral resources; therefore it is ranked sixth in the world in terms of estimated mineral resources [6].

Kazakhstan is rich in coal, oil, natural gas, and uranium with estimated reserves containing 31.3 billion tons, 3.9 billion tons, 2.4 trillion m^3, and 62.9 billion tons, respectively [7].

The country is significantly dependent on fossil fuels for its energy utilization. Kazakhstan's energy production covers more than twice its energy demand, and the energy self-sufficiency is rated at around 200 % (Fig. 4). Coal represents almost 50% of the primary energy supply of Kazakhstan (Fig. 5), and it is utilized for domestic energy consumption, while natural gas and oil are for exports [8].

The total production of all-electric energy is 101000 GWh, which is 107% of the country's usage. Coal consumption for electricity production is estimated by more than 70% of total power generation (Fig. 6) [9]. However, the currently existing infrastructure is disintegrating, and new construction is unfeasible because of a complicated political situation.

Approximately 50% of generators have run for more than 30 years. At most 30% of the heat is lost during transportation and distribution. The current state of the electricity and heating system shows that it is necessary to resolve issues of reducing wear and tear on equipment of power plants and networks [10].

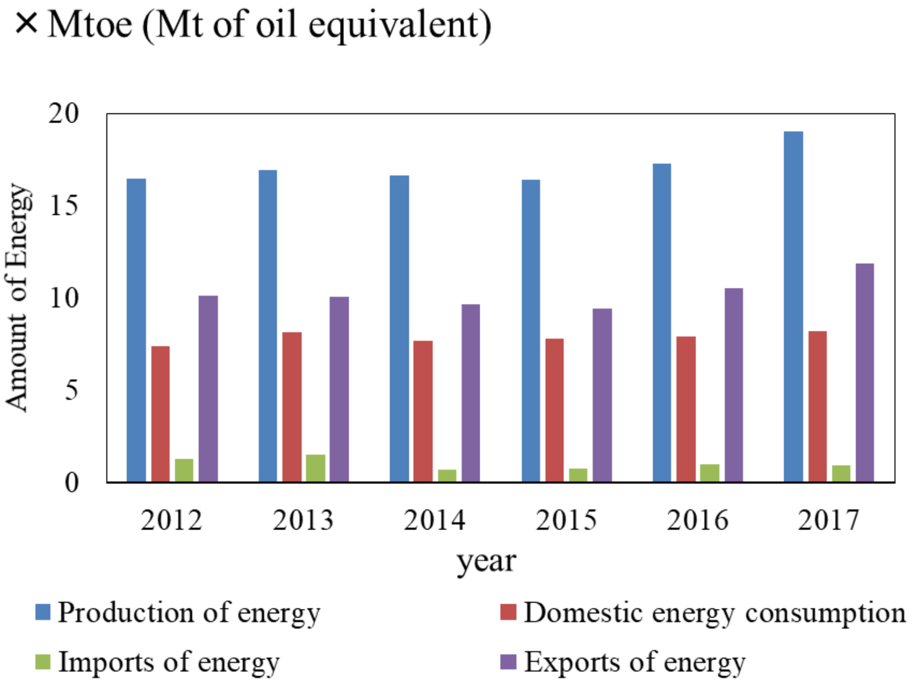

Fig. 4 Total production and consumption of energy (2012-2017) [8]

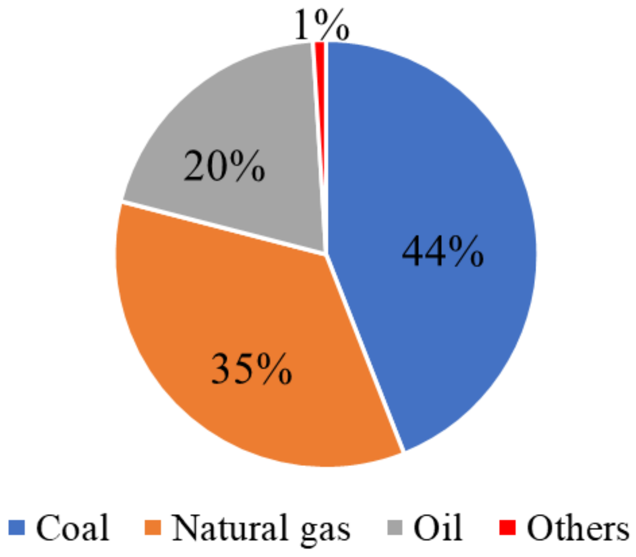

Fig. 5 Primary energy supply in Kazakhstan (2017) [8]

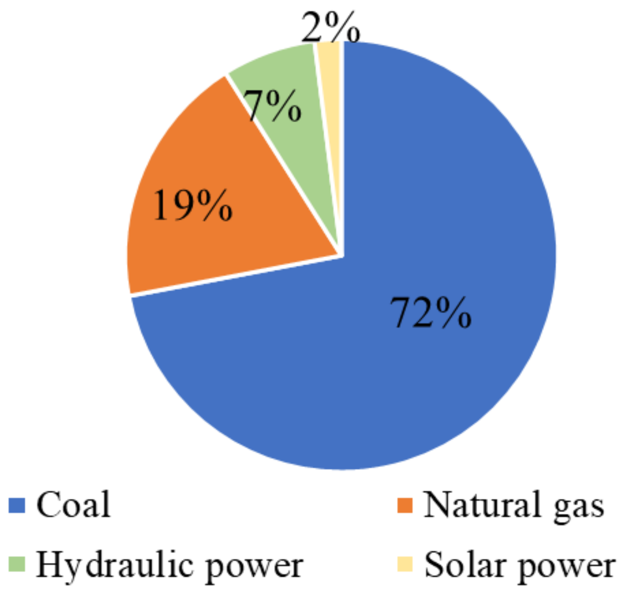

Fig. 6 Electric power supply in Kazakhstan (2017) [9]

The industry sector is the primary driver of final energy consumption in Kazakhstan (Fig. 7). The industry uses coal as the primary energy source. The housing sector is the second-largest final energy-consuming sector, and oil is mainly used for transport purposes [8].

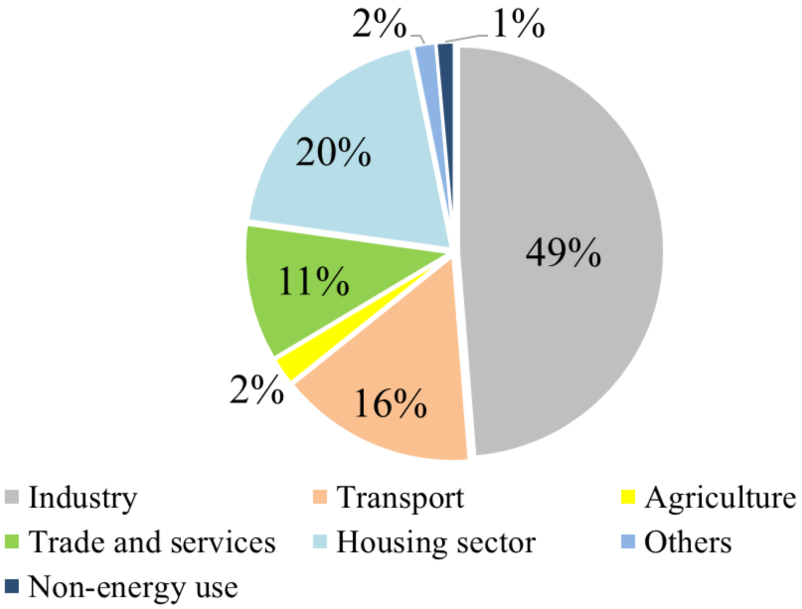

Fig. 7 Final energy consumption by sectors (2017) [8]

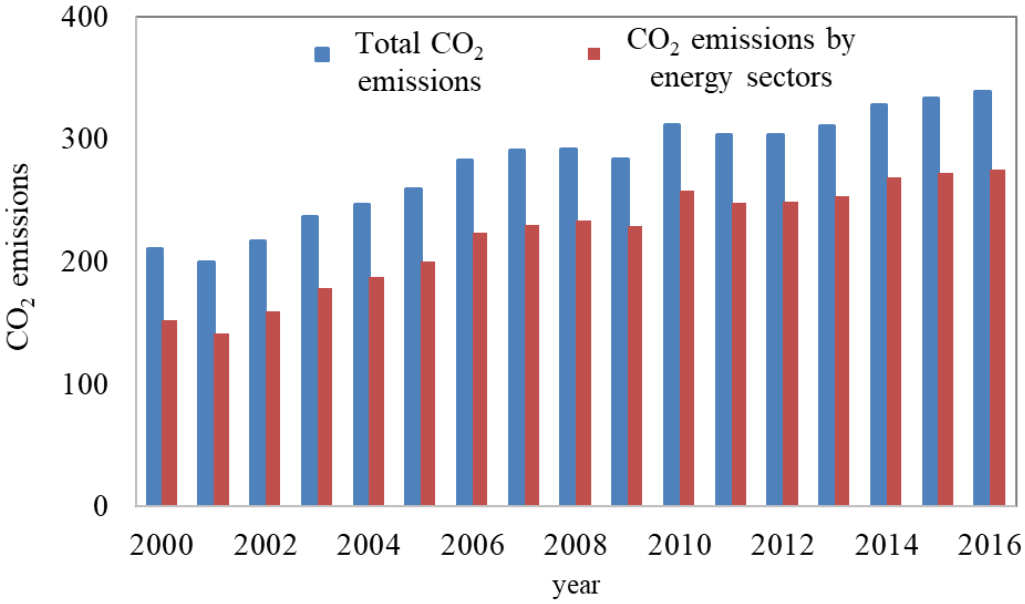

Fig. 8 CO_2 emissions (2000-2016) [8]

However, poor quality coal with low average efficiency levels in energy use has been the most important source of greenhouse gas emissions, representing 80% of total emissions in 2010 (Fig. 8) [8].

According to the International Energy Agency, the energy production, total energy supply, final electricity consumption, and CO_2 emissions increased from 2000 to 2017 by 127.85%, 136.41%, 95.74%, 128.57%, respectively, which shows increasing in energy consumption and impact on the environment [11].

1.4. Renewable energy resources and potential

Kazakhstan has considerable renewable energy potential, mainly in the form of wind and solar energy. Despite the current low consumption rate of renewables, excluding hydropower, which is 2% of all power generation, Kazakhstan has a high potential for power generation by renewable resources. This potential of renewable energy is available to supply all increasing demand and export of electricity, while promoting the reduction of CO_2 emission [12]. 119 renewable energy projects with 2096 MW of capacity were planned to develop renewable energy in Kazakhstan by 2021 (Table 2) [13].

Table 2 Number of projects of renewable energy in Kazakhstan [13]

Year	Number of projects of renewable energy	Technical capacity, MW		
2014	35	177		
2019	74	679	Hydropower	200.3
			Wind power	227
			Solar power	250
			Biomass	1.3
2020	95	1483		
2021	119	2096		

Primarily, we will focus on one of the promising areas of renewable energy to solar power. For example, Kazakhstan's southern and central regions have high insolation that could be suitable for solar power with daylight hours of 2200-3000 h/year and sunlight 1.3-1.7×10^3 kWh/m^2 annually (Fig. 9) [14]. Solar power could reach the range of 2.5-3.5×10^{12} kWh per year, 25 times larger than the current total production of electricity, and would use only half of the country's total surface area. With all these possible resources ready within its borders, Kazakhstan can develop sustainably.

The Atlas of Solar Resources of Kazakhstan has been created within the Project of Kazakhstan's Ministry of Energy and the United Nations Development Program. This project assists the Government of the Republic of Kazakhstan to implement the Green Economic Transition Concept of the Republic of Kazakhstan and institutionalize the Green Bridge Partnership Program [15].

Kazakhstan is now producing silicon photovoltaic cells. Astana Solar LLP (Limited Liability Partnership) is a subsidiary of Kazatomprom JSC (Joint Stock Company), which is the national operator of the Republic of Kazakhstan for the import and export of uranium, rare metals, and nuclear fuel for nuclear power. This company is working on a project for the production of photovoltaic modules using Kazakhstani silicon KazPV. The project aims to create a cycle of photovoltaic modules with full vertical integration, from the production of silicon to the construction of solar panels [16].

Kazakhstan needs sustainable development and aims to bring renewable energy in electricity generation to 30% by 2030 and 50% by 2050 [17].

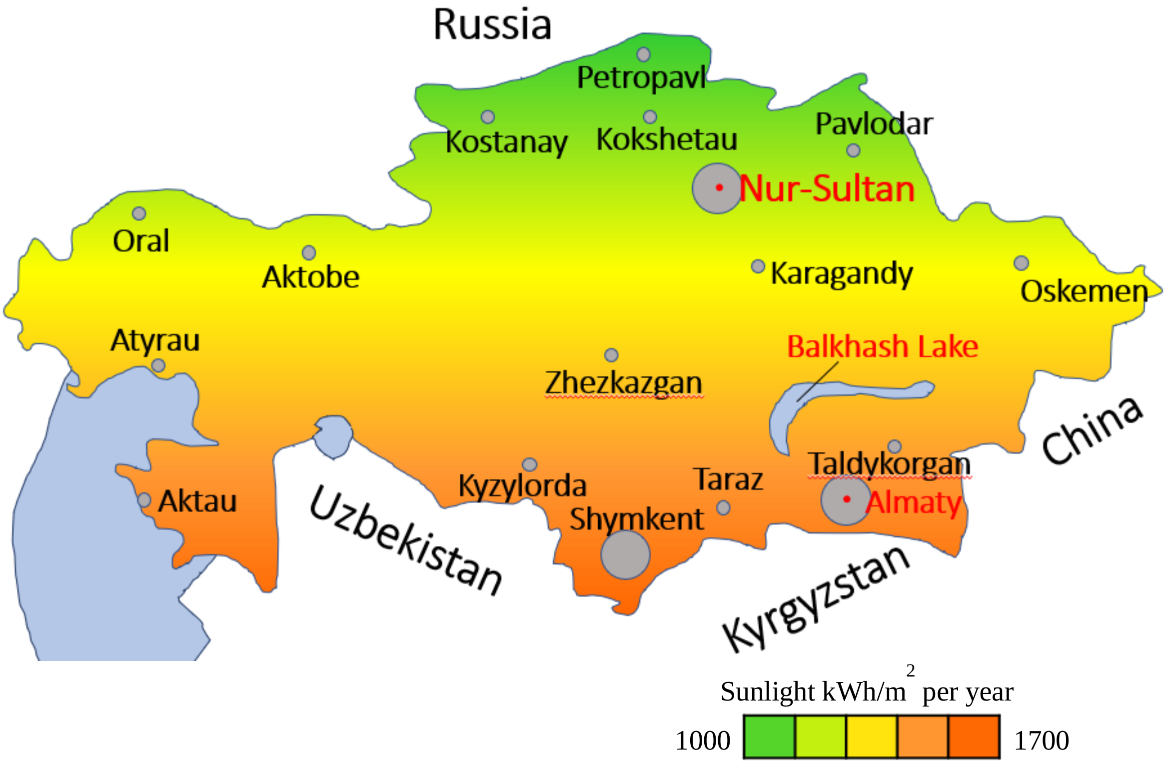

Fig. 9 Solar radiation [14]

1.5. Water resources issue

In exchange for plentiful sunshine, water resources in Kazakhstan are not abundant, because of climate characteristics such as deficient annual precipitation and desertification. The country's rainfall amount is not large, with the average annual precipitation estimated at around 250 mm. Water availability in Kazakhstan is 37000 m^3/km^2 and 3650 m^3/capita a year, an amount that is lower than the world’s average of 6000 m^3. Furthermore, it is expected that water availability will decrease to 2300 m^3/capita in a year by 2030 through desertification [18].

In Kazakhstan, water resources are mainly concentrated in eight major rivers basins (Ili, Irtysh, Ishim, Shu, Syrdaiya, Tobol, Talas, and Ural) and three big lakes (the Caspian Sea, Aral Sea, and Balkhash Lake). Balkhash Lake is the primary source of freshwater.

Water availability across these major basins is distributed unevenly, and approximately 45% of the water in the country inflows from neighboring countries such as Russia, China, Kyrgyzstan, and Uzbekistan (Fig. 11) [19]. Changes in withdrawals in any of the upstream countries are likely to have a very significant impact on the availability of water in Kazakhstan. For example, inflows are expected to decrease from 44.64 km^3 per year to 31.6 km^3 per year by 2030 due to increased water withdrawals for hydroelectricity generation and irrigation in countries in Central Asia and China [20].

Fig. 11 Transboundary rivers of Kazakhstan [19]

Annual freshwater withdrawals are around 2.3×10^{10} m^3/year total. Almost all freshwater is gathered from surface water because of a lack of groundwater. Consequently, surface water needs to be transported. Unfortunately, 12% of it is lost during transport due to old structures (Fig. 12) [8]. The average efficiency of canal water delivery systems is only 15-20% compared to 70-90% in most developed countries.

The water supply service is relatively weak in terms of quantity and quality. A shortage of high-quality drinking water is still acute in some regions, where households in remote areas have the water delivered in water tanks and stored in individual reservoirs.

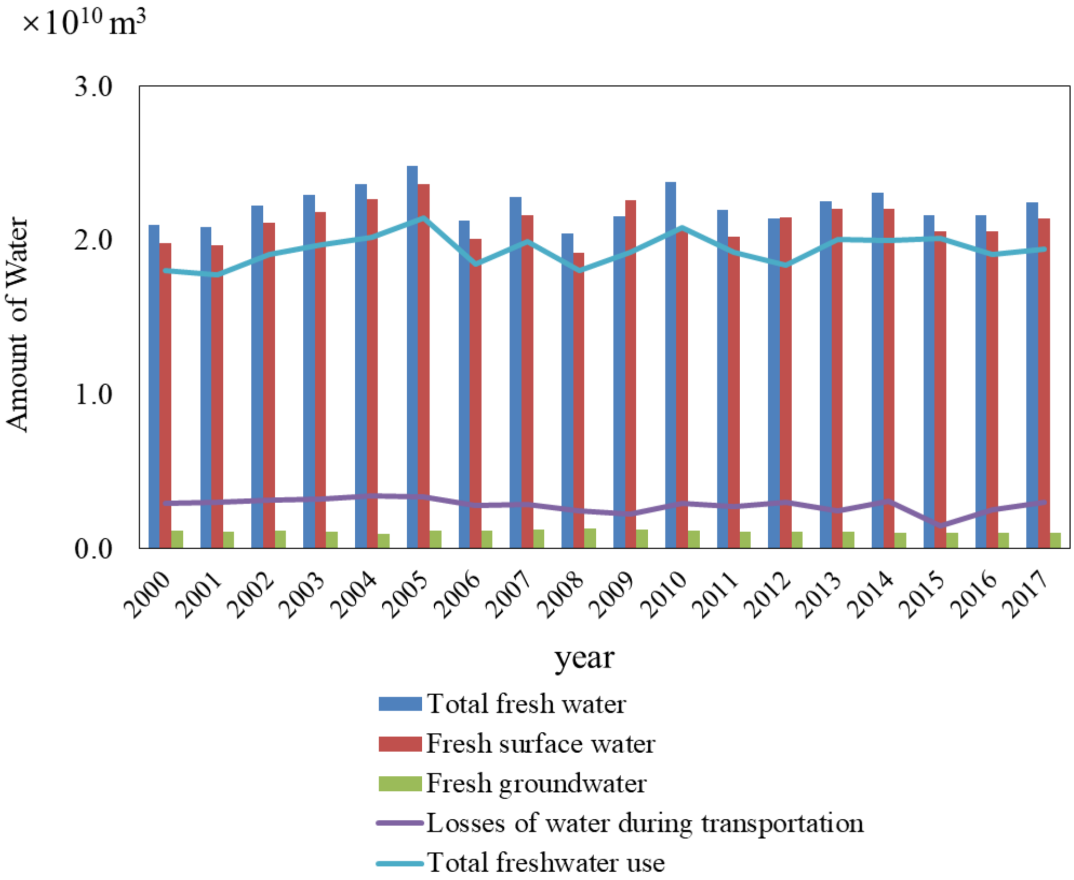

Fig. 12 Total freshwater abstracted, total freshwater use and losses of water during transportation (2000-2017) [8]

Moreover, tap water is not safe to drink in Kazakhstan, and around 30% of consumers completely abandon it, preferring to buy bottled water. Hence, 9×10^5 m^3 per year of bottled water is transported in large cities [21].

The agriculture sector is the primary driver of water consumption in Kazakhstan, which is approximately 70% of total consumption. The electricity industry and manufacturing are the second largest water-consuming sectors at 20% followed by households and others at 10% (Fig. 13) [8].

As we see, Kazakhstan has a water resources problem, namely a shortage of them, because of climate characteristics such as deficient annual precipitation and desertification. Hence, Kazakhstan has faced geopolitical tensions due to transboundary river use. However, the quantity of water resources is not the only big issue. Kazakhstan needs to consider the quality of transportation and supply to focus on water management too. Kazakhstan has developed National Water Programs such as "Ak Bulak" 2010-2020, National Water 2050 Strategy, and a State Program on Water Resources Management [19].

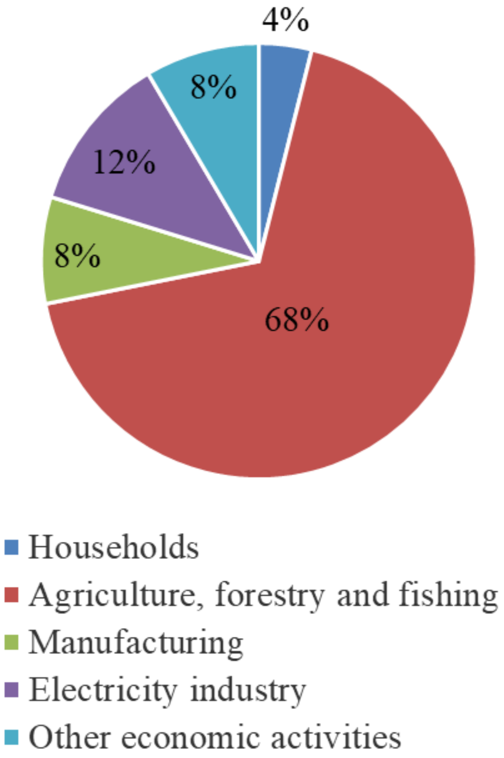

Fig. 13 Final water consumption (2017) [8]

1.6. Materials for hydrogen storage alloys

Kazakhstan has substantial natural and mineral resources. Out of the 110 elements in Mendeleyev’s periodic table, 99 have been discovered, 70 explored, and 60 are being extracted and used in Kazakhstan [6].

Metallurgy and mining are two main keys of industries, accounting for over 9% of GDP and circa 18% of total industrial production. About 80% of all mining industry products are exported to over thirty countries worldwide, representing 20% of total exports and 30% of the country's annual revenue [22].

Specifically, Kazakhstan has 30% of the global reserves of chrome ores, which is second globally, 25% of manganese ores, 10% of iron ores and is ranked tenth in the world in terms of titanium reserves (Table 3) [6]. Hence, their prices are lower than typical materials for hydrogen storage and metal resources capable of being utilized for hydrogen storage alloys.

Table 3 Kazakhstan reserves of metal resources with their world ranking rates and estimated cost [6]

Metal	World Ranking	Confirmed Reserves ($\times 10^7$ kg)	Cost US - $/kg	Global reserves (%)	Located part of Kazakhstan
Ti	10	2.40	4.8	0.1	East
Cr	2.0	38.2	5.1	30	West
Mn	4.0	63.5	2.0	25	Central
Fe	7.0	26.5	1.1	10	North

1.7. The purpose of the study

The study's purpose is to develop a hydrogen energy system in Kazakhstan for water supply, renewable energy distribution, and reduction of greenhouse gas emissions. This study considers the energy and water situation in Kazakhstan, which is currently significantly dependent on fossil fuels, despite the high potential of renewable energy sources, especially solar energy. Due in part to the abundance of sunshine, there are not many water resources in Kazakhstan.

This is the first research that supposes the role of the transportation of water by hydrogen. We propose a simple hydrogen energy system model as a solution for the water supply issues in Kazakhstan by utilizing the existing infrastructure as much as possible while considering cost and realizing the period.

The transportation can be driven by hydrogen production through electrolysis and hydrogen consumption through fuel cells, as proposed in the frame of the hydrogen energy system.

We propose a model of a possible hydrogen energy system with hydrogen production, storage, transportation, and utilization system for water transportation. Furthermore, we focus on an optimal, safe, effective, realizable method that will allow for hydrogen storage and transportation. We consider the transportation of Ti-based hydrogen storage alloy via railway. Materials for Ti-based alloys are abundant in Kazakhstan with low cost and rail is the main form of transport, which connects all of Kazakhstan.

In order to prepare Ti-based hydrogen storage alloy, we focus on MA (Mechanical Alloying) method, which provides mass production by accessible equipment. MA can synthesize various non-equilibrium alloys, so it has been widely applied to modify properties of a hydrogen storage alloy. Moreover, we investigate the hydrogenation and activation characteristics, and the effect of a catalyst on the Ti-based alloy prepared for mass production on an industrial scale. Therefore, we compare Ti-based hydrogen storage alloy prepared by Ti and TiH_2 as a starting material and consider optimal method of preparation.

Finally, we will check the amount of greenhouse gas production of the modeled hydrogen system in Kazakhstan by LCA (Life Cycle Assessment) analysis. We try to confirm that the considered hydrogen system is an ideal energy carrier and water supply system for other countries with water scarcity problems.

1.8. Organization of the thesis

The thesis is organized into 7 chapters; a brief outline of the thesis is as follows:

Chapter I. This chapter describes the research background, which is related to SDGs in Kazakhstan. The chapter also provides an overview of Kazakhstan and energy, water resources problems, and renewable energy potential. Subsequently, it discusses the research purposes and scopes.

Chapter II. This chapter describes hydrogen transportation methods and mentions methods of transportation by hydrogen storage alloys via railways.

Chapter III. This chapter proposes hydrogen energy as an alternate, new, sustainable, affordable, and reliable energy, as well as a drinking water supply source. Transportation of water can be driven by the production of hydrogen through electrolysis and the consumption of hydrogen through the use of fuel cells, as proposed in the frame of the hydrogen energy system.

Chapter IV. This chapter describes the activation characteristic of Ti-based alloy prepared for mass production. Moreover, the effect of addition Mn and catalyzer Pd/Al_2O_3 for oxidation.

Chapter V. This chapter describes the preparation of Ti-based hydrogen storage alloys and start materials such as Ti and TiH_2. Furthermore, it experimentally shows the optimal method of preparation by mechanical alloying

Chapter VI. This chapter shows the result of analyzing the environmental impact of the hydrogen energy system by LCA. The LCA result confirms that hydrogen is considered to be an ideal energy carrier in the future and can play a considerable role in the energy system.

Chapter VII. This chapter is devoted to conclusive remarks with some scope of future work.

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Chapter II: HYDROGEN ENERGY SYSTEM

2.1. Hydrogen energy system

This study proposes hydrogen energy as an alternate, new, sustainable, affordable, and reliable energy and a drinking water supply source by utilizing hydrogen energy using fuel cells.

Since renewable energy is unstable and large-scale electricity storage is not easy to handle at room temperature, to store excess electricity or supply it during the shortage, alternative energy storage methods are needed. One such alternative is hydrogen, a new energy resource that can store energy for an extended period, even though batteries have limited lifetimes.

Hydrogen has potential as a low-carbon energy source when it is produced from renewable energy. Hydrogen is the lightest gas on earth and the most abundant chemical substance in the universe. It has a very high energy content by weight, shallow energy content by volume, and burns faster than regular gasoline. It is 3.2 times less energy-dense than gasoline. Hence, hydrogen proves to be an energy carrier [1]. The benefits of using hydrogen as energy are the reduction of the amount of energy consumption, decarbonization of fuels, and promotion of the use of renewable energy. Therefore, currently, hydrogen has attracted a great deal of application as an ideal global energy carrier.

In 2018, hydrogen maintained its extraordinary current force, with over 20 MW of electrolyzer capacity coming online, and larger projects announced (up to 100 MW, mostly in Europe). All six new Carbon Capture and Storage project announcements in Europe related to hydrogen. Remarkable policies in France and Korea, plus high-level co-ordination by Japan, where government interest has increased. China raised its intention for/interest in vehicle production to globally significant levels [2].

The term “Hydrogen Economy” refers to the infrastructure which is used to support the energy requirements of society based on the use of hydrogen in place of fossil fuels. The hydrogen economy is highly beneficial for society as it will lead to the opening of new industries to produce materials along with changes in vehicle power sources, which would finally result in reduced pollution levels [3].

In order to create a hydrogen energy system, a practical consideration is especially needed regarding hydrogen production, storage, and utilization that does not have a large impact on the environment. For the realization and prosperity of a hydrogen energy society, hydrogen should be produced by renewable energy sources. However, this depends on climatic conditions, location and population, energy consumption, and whether the system would be comprised of wind and photovoltaic renewable technologies or both [4-16].

Particularly, hydrogen production by photovoltaic technology is supposed to be much more practical. The utilization of the enormous energy potential of solar radiation and its effective conversion to chemical energy carriers, such as hydrogen, is a subject of primary technological interests. The first solar-hydrogen system was applied in 1986 and reported by researches and operated in countries such as Germany [4], Switzerland [5], Spain [6, 13], Mexico [7], the USA [8], China [9], Italy [11, 14], Japan [12, 16], etc.

This system was verified as effective energy storage for countries leading the way in renewable energy. Integration with photovoltaic power sources in a local direct current grid acquires a regularly stable energy source. Moreover, the solar-hydrogen system can provide large capacity high-quality emergency power supply, where there are frequent occurrences of extreme weather events and large natural disasters. Therefore, a long-time reliable autonomous emergency power supply when outages or shortages happen is obtainable in Japan [16]. Isolated areas such as islands, which completely depend on the import of fossil fuels for energy production, will find a solution through renewable energies using hydrogen as a water and energy self-supply by using for water desalination such as in Spain [13].

In order to create a hydrogen energy system, we need a practical consideration of hydrogen production, storage, and utilization that does not have a significant impact on the environment [3].

For the realization and prosperity of a hydrogen energy society, it is essential to recognize that its production method plays a significant role in environmental impacts. Hydrogen produced from water using renewable energy sources, called "green hydrogen," offers the prospect of long-term growth in full alignment with the need to protect the environment. It will be one of the most promising energy options for a sustainable future [17]. Cycling of hydrogen without CO_2 emissions can be achieved by producing hydrogen by electrolysis and hydrogen consumption through fuel cells.

Nowadays, the technologies for the production and use of hydrogen have been found, and efficiency and cost problems have been identified. According to the experts, hydrogen produced via PV electrolysis at prices under US$ 2/kg by 2030 shows the potential of realizing hydrogen society is increasing [18]. Also, to use hydrogen in practice, it is necessary to consider a reliable and stable method of storing and transporting it.

2.2. Hydrogen storage and transportation methods

The development of an appropriate hydrogen storage technique is one of the most critical problems of hydrogen energy. Hydrogen can be stored and transported by different methods from the point of production to the point of use. The primary method is physical storage when hydrogen is stored in cylinders as a compressed gas or cryogenic liquid. Another way is a chemical method when hydrogen is being chemically bonded with a storage material. Currently, hydrogen is stored and transported as gaseous and liquid hydrogen via pipeline, over the road in cryogenic liquid tanker trucks, or gaseous tube trailers.

2.2.1. Gaseous hydrogen

First, gaseous hydrogen has a very high energy density per weight. However, its energy density per volume is small. For example, at standard temperature and pressure it has a low density of 0.089 $g \cdot L^{-1}$. About 5 m in diameter, a spherical volume is necessary for 6 kg of hydrogen gas. The common practice is to pressurize hydrogen gas into a steel cylinder based on the PVT (Pressure, Volume, Temperature) characteristics. For the present, high-pressure tanks have been rated to a maximum of 700 bar. Even with such high pressures at 700 bar, 6 kg of hydrogen still requires a storage tank with about 150 L capacity [19]. Moreover, the transportation of gaseous hydrogen still has some unsolved issues.

Gaseous hydrogen is compressed to pressures of 180 bar or higher into long cylinders stacked on a trailer that the truck hauls. Trucks that carry gaseous hydrogen are called tube trailers. Tube trailers are currently limited to pressures because of safety. Moreover, due to the heavyweight of the steel tubes there is a limited carrying capacity for on-road vehicles [20].

Currently, gaseous hydrogen can be transported through pipelines in the same way as natural gas. A pipeline network is also an option for the general and largescale use of hydrogen as an energy source. However, pipelines require high initial investment levels and long-term construction. Design requirements for hydrogen pipelines are still evolving. Most hydrogen pipelines are designed to transport hydrogen only for short distances, from the production facility to the end-user.

Moreover, the hydrogen pipeline quickly develops leaks, requiring strict safety equipment and carries only about 80% energy at the same pressure as natural gas [21].

Hydrogen pipelines have problems with embrittlement, safety, and leaks. Hydrogen has an active electron, and therefore behaves somewhat like a halogen. For this reason, hydrogen pipes have to resist corrosion in the ground. The problem is intensified because hydrogen can easily migrate into most metals' crystal structures [22].

2.2.2. Liquid hydrogen

The second well-known method is liquid hydrogen. Hydrogen is most commonly transported and delivered as a liquid when high-volume transport is needed. Liquid hydrogen systems offer a higher density of $71 g \cdot L^{-1}$ H_2 at 20.15 K. Liquid hydrogen is reduced in volume by 1/800 compared with gaseous hydrogen [19]. However, the heat input from the surrounding into the tank leads to hydrogen evaporation called the boil-off phenomenon, especially when using small tanks with large surface-to-volume ratios. The currently available engineering technologies have not yet been able to prevent the heat input from the environment and suppress those losses. Liquefaction consumes more than 30% of the energy content of the hydrogen and it is expensive [20].

Nowadays, for longer distances, hydrogen is transported as a liquid in super-insulated, cryogenic tanker trucks. After liquefaction, the liquid hydrogen is dispensed to delivery trucks and transported to distribution sites vaporized to a high-pressure gaseous product for dispensing. Over long distances, trucking liquid hydrogen is more economical than trucking gaseous hydrogen. However, there are energy and cost problems for liquefaction, low boiling point, superior heat insulation, and boil-off.

Additionally, research and analysis are underway to investigate novel hydrogen carriers stored in some other chemical state, rather than as free hydrogen molecules, which are still in the research and development stage and are not yet energetic or cost-efficient.

Currently, the organic chemical hydride (OCH) method by methylcyclohexane (MCH) produced from toluene and hydrogen is mentioned for storing and transporting hydrogen. Toluene and MCH are maintained in a liquid state at ambient temperatures and pressures, which can be stored and transported at a compressed volume of approximately 1/500 as hydrogen at ambient temperature and pressure [23].

2.2.3. Metal hydrides

Potential carriers include metal hydrides, carbon or other nanostructures, as well as reversible hydrocarbons or other liquids. The use of such novel carriers would constitute a significant impact on the spread of hydrogen utilization. However, we considered hydrogen storage alloys as promising hydrogen carriers for a safe and feasible solution in this research.

Metal hydrides are chemical compounds formed by hydrogen with several individual metal and intermetallic compounds. This method ensures the most compact and safe hydrogen storage due to the hydrogenation reaction's reversibility under mild conditions and the too-high hydrogen density in the metal hydrides. Moreover, the dissociation of the hydride leads to the release of hydrogen of high purity (99.9999%), which is especially important for applications in energy systems of fuel cells [20].

2.3. Hydrogen transportation by hydrogen storage alloy via railway

To make the usage of hydrogen practically, the development of transport and storage technology has focused on the development of highly safe hydrogen storage materials that have high hydrogen density and can absorb and release hydrogen by a simple operation of temperature or pressure. We considered hydrogen storage alloys as hydrogen carriers with high structural stability and hydrogen storage capacity in this contribution. Hydrogen storage alloys have attracted considerable attention because they are a safe and efficient media for transporting hydrogen energy. Since hydrogen storage alloys are heavy, they can be transported by rail safely, consequently increasing the amount of hydrogen transported in the existing infrastructure.

The load capacity of one freight car is 6-7×10^4 kg [24]. Additionally, railway transportation is attractive for its lower emission of CO_2. The amount of CO_2 emissions is 2.53×10^{-10} kg-CO_2/kg・m (25.3g/ ton・km) [25]. Furthermore, the transportation of hydrogen by units is easy to carry the required amount of electricity and water to the required place. If a fuel cell is attached to a locomotive, the train can supply energy by itself and distribute water along the rail lines.

For example, the world's first hydrogen-powered train started operating in Germany in 2018, and it can run for about 1000 km on a single tank of hydrogen, similar to the range of diesel trains [26].

2.4. Summary of chapter

This chapter introduces the hydrogen energy system. To create a hydrogen energy system, we need a practical consideration of hydrogen production, storage, and utilization that does not have a significant impact on the environment. Nowadays, the technologies for the production and use of hydrogen have been found, and efficiency and cost problems have been identified. Also, to use hydrogen in practice, it is necessary to consider a reliable and stable method of storing and transporting it.

The development of an appropriate hydrogen storage technique is one of the most critical problems of hydrogen energy. Hydrogen can be stored and transported by different methods from the point of production to the point of use. The primary method is physical storage when hydrogen is stored in cylinders as a compressed gas or cryogenic liquid. Another way is a chemical method when hydrogen is being chemically bonded with a storage material. Currently, hydrogen is stored and transported as gaseous and liquid hydrogen via pipeline, over the road in cryogenic liquid tanker trucks, or gaseous tube trailers.

To make the usage of hydrogen practical, the development of transport and storage technology has been focused on the development of highly safe hydrogen storage materials that have high hydrogen density and can absorb and release hydrogen by a simple operation of temperature or pressure. We considered hydrogen storage alloys as hydrogen carriers with high structural stability and hydrogen storage capacity in this contribution. Hydrogen storage alloys have attracted considerable attention because they are safe and efficient media for transporting hydrogen energy. Since hydrogen storage alloys are heavy, they can be transported by rail safely, consequently increasing the amount of hydrogen transported in the existing infrastructure.

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Chapter III: HYDROGEN ENERGY SYSTEM FOR WATER TRANSPORTATION (IN CASE OF KAZAKHSTAN)

3.1. Hydrogen energy system for water transportation

The overall hydrogen system consists of solar energy, an electrolyzer for hydrogen production, alloys for hydrogen storage, trains for transportation, and fuel cells for utilization.

In this research, the hydrogen energy system was modeled for a city with a population of one million based on a calculation per capita. They will consume hydrogen, which is generated by the electrolysis method from Balkhash Lake by utilizing solar power and transported by hydrogen storage alloys via railway.

We consider the fuel cell (50% efficiency for electricity) and simulated hydrogen energy system for the capital city Nur-Sultan, where the population is growing [1], and consumption of energy and water is increasing (Fig. 14).

The solar panel area will be located near Balkhash Lake because of high solar radiation in the South and Central part of Kazakhstan [2] (Fig. 14).

This lake was chosen because of the location and quality of water. Moreover, Balkhash Lake is the primary water resource in domestic supply. The volume of water in Balkhash Lake is 1.1×10^{11} m^3 [3]. The distance between Balkhash and Nur-Sultan is around 6×10^5 m and a railway between Astana and Almaty through Lake Balkhash [4] (Fig. 14).

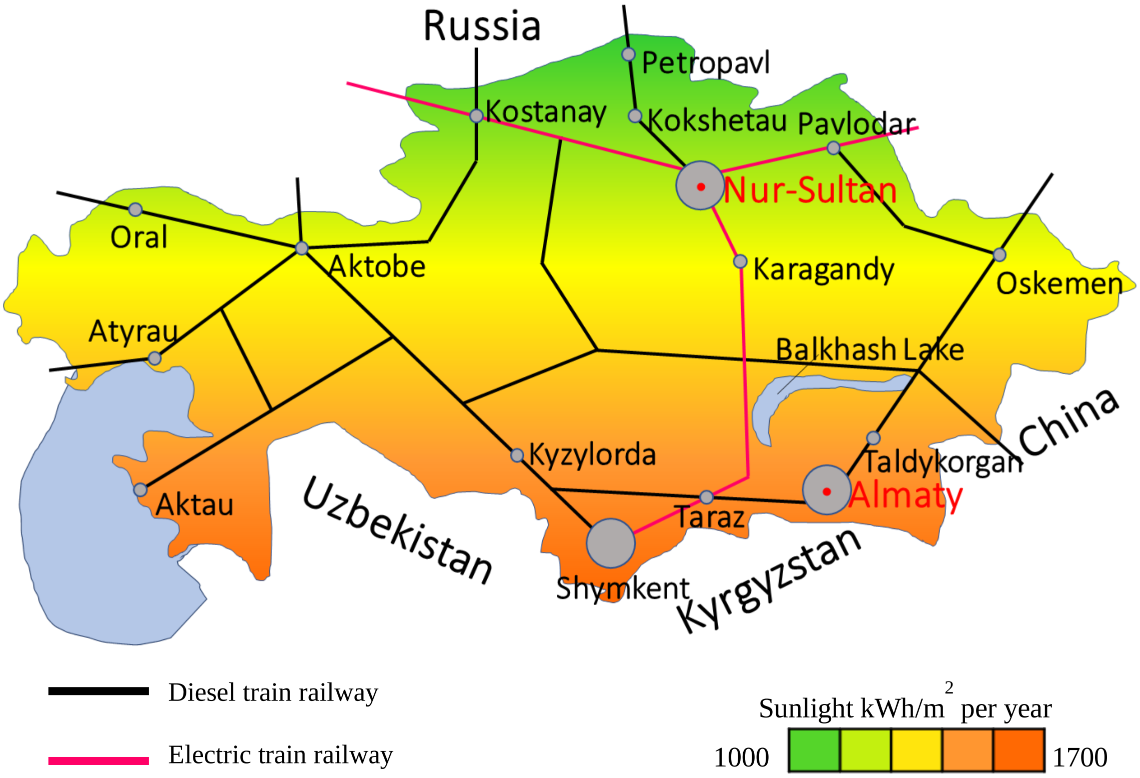

Fig. 14 Solar radiation, population density, railway map of Kazakhstan made based on references [1,2,4]

3.2. Hydrogen production by solar power via electrolysis

Renewable energy-driven hydrogen generation is a favorable method. Renewable energy can be used to generate electricity that can be used to produce hydrogen through water electrolysis. Given the climatic conditions of Kazakhstan, the available renewable resource is solar power.

The hydrogen energy system consists of an electrical energy generation plant using solar irradiation as prime energy resources. During periods of high electricity demand, the energy that is produced is fed into a stand-alone grid to supply the energy needs of the population. During low demand periods, the plant will use the surplus energy generated to produce hydrogen utilizing water electrolysis.

First, we consider the amount of hydrogen per capita as the necessary energy and the amount of water as the amount of hydrogen needed to be utilized.

The energy consumption per capita is 5.00×10^3 kWh/year (1 kWh = 1 J/s×3600 s = 3.6×10^6 J) and clean drinking water consumption per capita of 1 m^3/year in Kazakhstan [5]. We summarize the appropriately quantified analysis of the Hydrogen Energy System in Kazakhstan based on these amounts.

The corresponding hydrogen amount is calculated as follows of formula (1). We use Lower Heating Values (LHV) of hydrogen, which is 6.72×10^{-2} kWh/mol. (The lower heating value is the amount of heat released during the complete combustion of fuel without condensation of water vapor If it condensed, available energy is denoted as Higher Heating Values(HHV) [6].)

$$E_{\text{per capita}}\,(5.00\times10^3\,\text{kWh}) \,/\, LHV_{\text{hydrogen}}\,(6.72\times10^{-2}\,\text{kWh/mol}) = 7.44\times10^4\,\text{mol } H_2 \qquad (1)$$

7.44×10^4 mol H_2 produces 7.44×10^4 mol water, which is 1.34 m^3/year and provides the necessary amount of hydrogen to required electricity 5.0×10^3 kWh/capita.

To find the required energy to produce 1m^3 (44.64 mol) hydrogen we use Higher Heating Values (HHV) of hydrogen, which is 7.87×10^{-2} kWh/mol.

$$H_2\,(44.64\text{ mol})/\ \times HHV_{\text{hydrogen}}\,(7.87\times10^{-2}\,\text{kWh/mol})=3.51\text{ kWh} \qquad (2)$$

The result of equation (2) is 3.51 kWh, this is the necessary energy to produce 1m^3 of hydrogen.

From (1) we calculated the volume of hydrogen consumption per capita

$$7.44\times10^4\,\text{mol } H_2 \,/\, 44.64\,\text{mol/m}^3 = 1.66\times10^3\,\text{m}^3 \qquad (3)$$

By (2) and (3), we can calculate the necessary energy to produce hydrogen per capita.

$$3.51\,\text{kWh/m}^3\times(1.66\times10^3\,\text{m}^3) = 5.82\times10^3\,\text{kWh} \qquad (4)$$

The main production method of hydrogen is electrolysis. If the electrolysis apparatus from Norsk with around 70% (Table 4) of conversion efficiency is used, to get

5.9×10^2 kWh (4) of energy we have to find the necessary energy by electrolysis apparatus [7].

$$5.82\times10^3\ \text{kWh}\times100\%\ /\ 70\% = 8.31\times10^3\ \text{kWh} \qquad (5)$$

If solar power will be used to produce hydrogen, it requires solar panels for the electricity-generating capacity of 88.31×10^3 kWh (5). Kazakhstan's photovoltaic products from Astana Solar with 16% conversion efficiency will be used for calculation (Table 5) [8].

$$8.31\times10^3\ \text{kWh}\ \times100\%/\ 16\% = 5.19\ \times10^4\ \text{kWh} \qquad (6)$$

As mentioned before, the amount of sunlight in Kazakhstan is approximately 1300-1700 kWh/m^2 annually (Fig.14). The average solar radiation is 1.5×10^3 kWh/m^2.

To produce $5.19\ \times10^4$ kWh (6) of energy we calculated a required surface area of solar panels.

$$5.19\ \times10^4\ \text{kWh}\ /\ 1.5\times10^3\ \text{kWh/m}^2 = 34.6\ \text{m}^2 \qquad (7)$$

The energy consumption per capita in Kazakhstan is 5000 kWh/year, which can get by 7.44×10^4 mol (1.66×10^3 m^3) of hydrogen. To produce this amount of hydrogen we need 1.34 m^3/year of water, 5.82×10^3 kWh, which comes from an electrolyzer with 8.31×10^3 kWh of power consumption and $5.19\ \times10^4$ kWh of solar energy from solar cells with 34.6 m^2 of surface area.

Table 4 Characteristic of Norsk Hydro Electrolysers [7]

Conversion efficiency	70% (average)
Energy consumption	4.8 ±0.1 kWh/Nm^3
Atmospheric electrolyzer for capacities	50 Nm^3/h

Table 5 Astana Solar PV module characteristics [8]

Conversion efficiency	16%
Cell type	Polycrystalline 6 (156x156 mm)
Module configuration	6 columns x 12 cells
Dimensions	1,967x992x40 mm
Weight	28 kg

We determine the required energy to produce this amount of hydrogen. We calculated the necessary energy from the electrolyzer, solar power, and surface area based on efficiency, 70%, and 16 %, respectively. We obtain 1.34 m^3/year/capita water by a fuel cell, which ensures the necessary water 1 m^3/year per capita. . Calculated results per capita and 1 million (M) people are shown in Table.6.

Table 6 Calculation to produce the required energy and water by hydrogen

Process	Per capita	Per 1 M people
Necessary water to produce hydrogen	1.34 m^3/year	1.34×10^6 m^3/year
Solar power and surface area (16% energy efficiency)	5.19×10^4 kWh/year 34.6 m^2	1.04×10^{11} kWh/year 70×10^7 m^2
Energy from electrolyzer (70% energy efficiency)	8.31×10^3 kWh /year	16.7×10^3 kWh/year
Produced hydrogen	7.44×10^4 mol /year	7.4×10^{10} mol /year
Energy consumption per capita	5000 kWh/year	2.0×10^9 kWh/year
Produced water	1.34 m^3/year	1.34×10^6 m^3/year

3.3. Hydrogen storage and transportation by hydrogen storage alloy via railway

Produced hydrogen will be stored by Ti-based hydrogen storage alloys, since in Kazakhstan Ti, Cr, Fe, and Mn are abundant, and their prices are lower than rare earth metals.

As mentioned above, Kazakhstan has reserves of titanium, chrome, manganese ores, and iron ores ranked in the top tenth in the world reserves [9].

In this contribution, we consider utilizing those metals for hydrogen storage alloys as hydrogen carriers. In general, the titanium-based alloys are among the most promising materials for hydrogen storage [10]. Currently, practically useful hydrogen storage alloys are made from rare earth metals, rare resources and are very expensive. In Kazakhstan Ti, Cr, Fe, and Mn are abundant, and their prices are lower than rare earth metals.

According to the literature, TiCrMn and TiFeMn alloys absorb reversibly about 1-1.5 wt% of hydrogen on average (Table 7) [11-16]. Alloys TiCrMn, TiFeMn are suitable as capable carriers for the transport of hydrogen energy in Kazakhstan.

We suggest preparing a hydrogen storage alloy by mechanical alloying (MA) technique, which is a more suitable manufacturing method for alloys' mass production.

MA can synthesize various non-equilibrium alloys, so it has been widely applied to modify properties of a hydrogen storage alloy. Compared with the arc melting (AM) method, the MA method enables synthesizing at low power for a long time. We will consider the preparation of alloys by MA in our next chapters.

Table 7 The hydrogen storage characteristics of Ti-based alloys [11-16]

Alloys	T (K)	P (MPa)	H (wt%)	Preparation	Ref.
$Ti_{1.1}CrMn$	296	3.30	1.80	AM	[11]
$TiCrMn_{0.8}$	304	1.00	1.98	AM	[12]
$Ti_{1.1}CrMn$	273	1.20	1.61	AM	[13]
$TiFe_{0.8}Mn_{0.2}$	298	1.50	1.65	AM	[14]
$TiFe_{0.9}Mn_{0.1}$	295	0.80	1.50	AM	[15]
$TiFe_{0.85}Mn_{0.15}$	298	1.50	1.20	MA	[16]

An essential transport mode in Kazakhstan is railway transport, which connects the entire country (Fig. 14). Trains account for 68% of all cargo and passenger traffic, covering over 57% of the country's territory. The load capacity of one freight car is 6-7×10^4 kg [17-18].

We assume the weight of transported hydrogen storage alloy per wagon is 5.4×10^4 kg with 1.5 wt% of hydrogen. The hydrogen capacity per wagon is 4.1×10^5 mol.

If a regular train is composed of 50 wagons, 2.04×10^7 mol H_2 will be transported. If a train transports it 10 times per day, they transport 2.04×10^8 mol of H_2/day and 7.4×10^{10} mol /year. Approximately 3×10^7 kg/year of the alloy will be used (Table 8).

Table 8 Calculation to transportation of alloy and hydrogen

Transporation	Alloy (kg)	Hydrogen (mol)
1 wagon	5.40×10^4	4.10×10^5
1 train (50 wagons)	2.70×10^6	2.04×10^7
Per day (10 times)	2.70×10^7	2.04×10^8
Per year	9.80×10^9	7.44×10^{10}

3.4. Hydrogen utilization by a fuel cell

The hydrogen energy system for water transportation is available by utilizing fuel cells for hydrogen utilization. This system is capable of satisfying drinking water requirements, and each citizen can become practically self-sufficient.

In this system, we can consider 3 types of fuel cells on 3 different scales (Fig. 15). On a large scale, one a considerable hydrogen station can provide electricity and water to citizens, controlled and dependent by the local administration. Transported hydrogen by hydrogen storage alloy via railway is available to obtain with hydrogen directly.

Secondly, each building can independently set a fuel cell for a medium scale and provide hydrogen to each apartment. For this, the hydrogen storage alloy can be transported in a unit form, such as a tube. The integral unit of hydrogen is available to be transported. The system is working in a half independent way.

Finally, the independent system for individuals is available too. Each citizen can buy small scale fuel cell apparatuses for their own house and purchase hydrogen storage alloys in several amounts using a small tube depending on his electricity and water consumption.

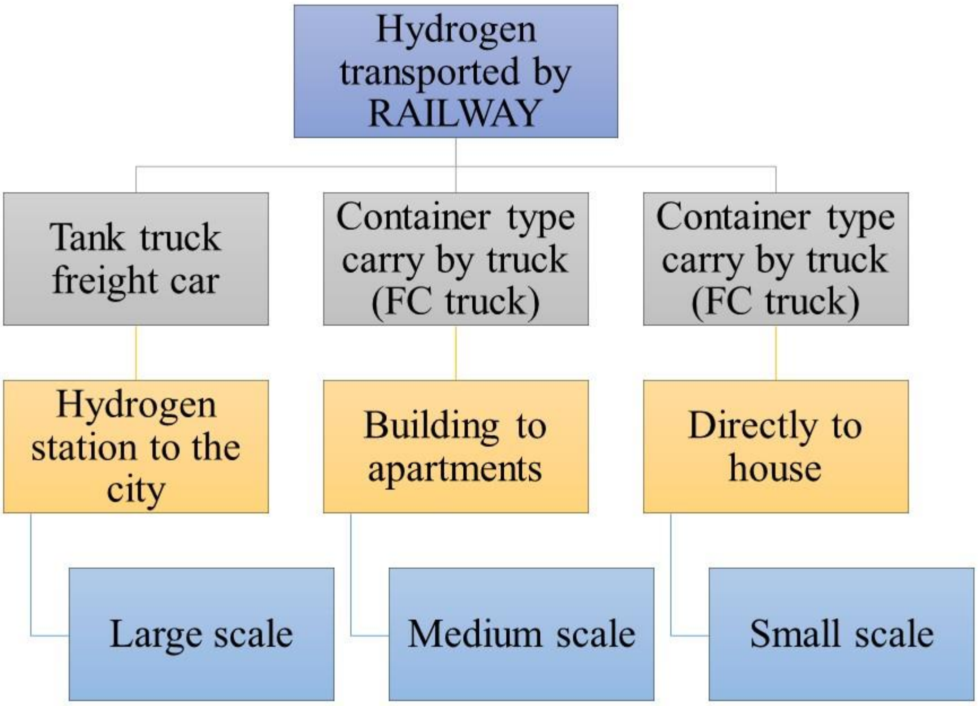

Fig. 15 Utilization of a fuel cell system for Hydrogen Energy System

Moreover, we considered methods of hydrogen distribution to fuel cells. In order to obtain hydrogen from hydrogen storage alloy transported by railway (Fig. 16):

1) The withdrawal of hydrogen from hydrogen storage alloy by a pump and distribute to FC.
2) The withdrawal of hydrogen storage alloy from a wagon.

By those 2 methods, hydrogen can be obtained safely with the required amount to utilization.

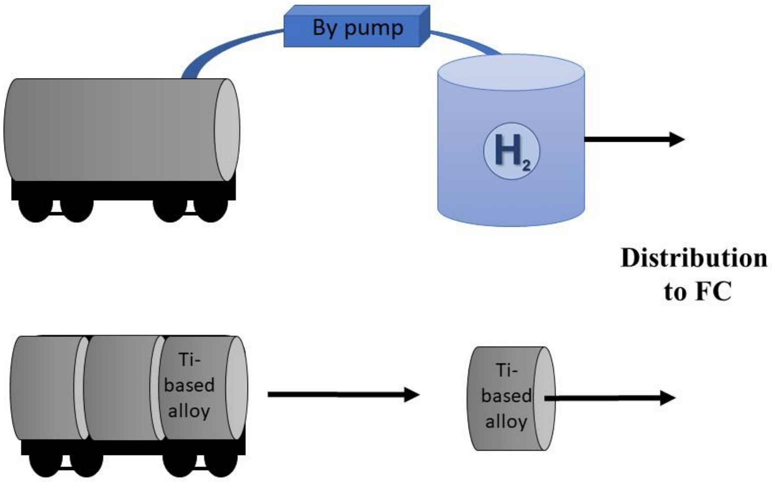

Fig. 16 Withdrawal of hydrogen from hydrogen storage alloy tank transported by railway

As mentioned before, the Hydrogen Energy System for Water Transportation is considered for the capital city Nur-Sultan with one million people population. Hydrogen will be produced by water electrolysis. The amount of necessary water to produce hydrogen is 1.3×10^6 m^3/year for one million people. Water will obtained from Balkhash Lake, which is a clean water resource.

The result of our research shows the high potential of solar power in Kazakhstan.

By utilizing 1.0.4×10^{11} kWh/year of solar power and 70×10^{7} m^2 surface area (16% energy efficiency) we will have the energy to the electrolyzer. Energy from electrolyzer (70% energy efficiency) is 16.7×10^{3} kWh/year, which produces 7.4×10^{10} mol of hydrogen. 7.4×10^{10} mol of hydrogen by a fuel cell (50% efficiency) produces 2.0×10^{9} kWh/year of electricity and 1.3×10^{6} m^3/year of water.

1.3 million people are provided with water and 0.4 million people with electricity by utilizing fuel cells. The total values are summarized in Fig. 17 [19].

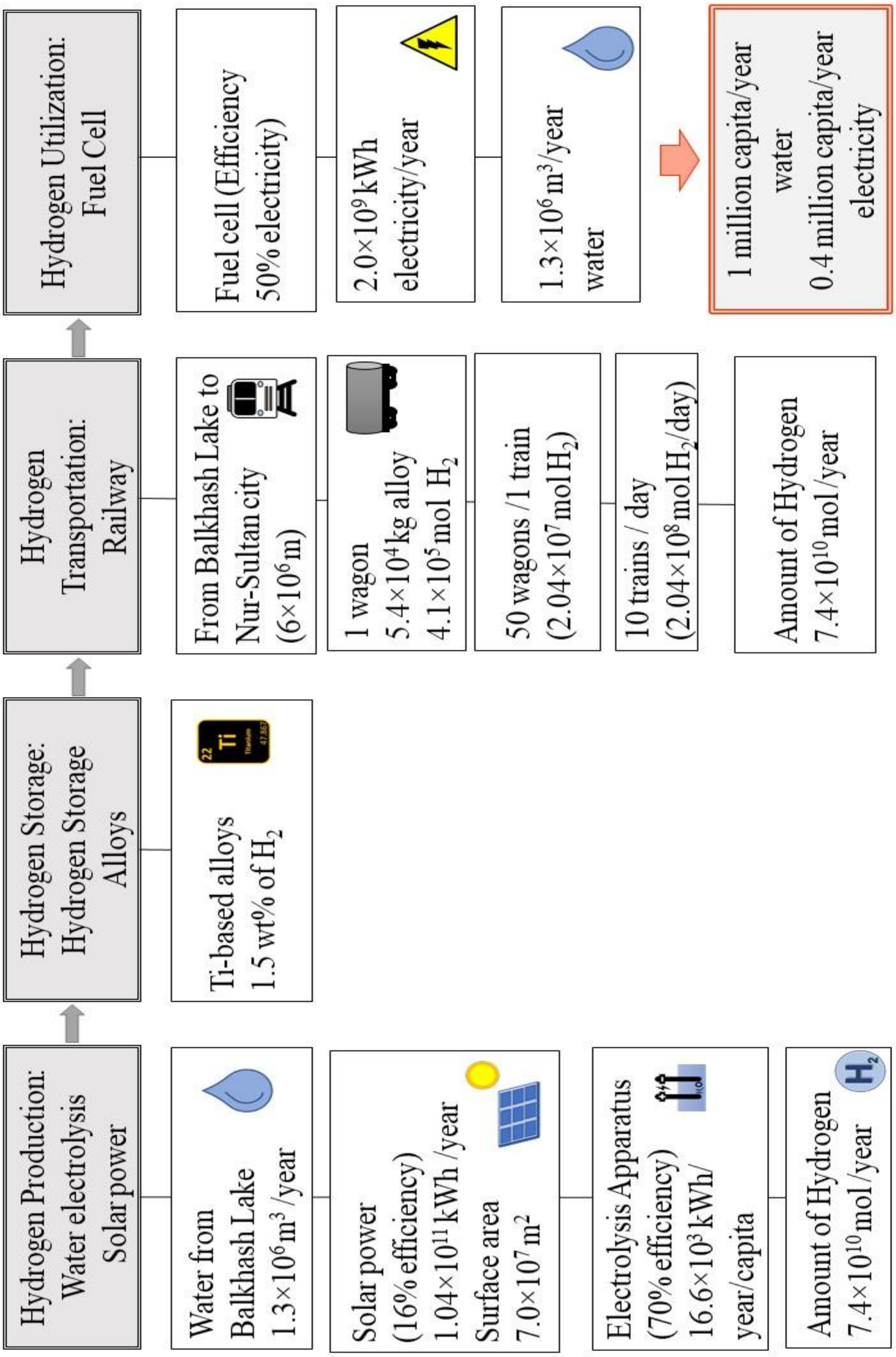

Fig. 17 Hydrogen Energy System for Kazakhstan [19]

3.5. Summary of chapter

This study proposes hydrogen energy as an alternate, new, sustainable, affordable, and reliable energy, as well as a drinking water supply source by utilizing hydrogen energy using fuel cells. As a first feasibility study, we propose a simple hydrogen energy system model as a solution for the water supply issues in Kazakhstan by utilizing the existing infrastructure as much as possible while considering cost and implementation period.

Transportation of water can be driven by the production of hydrogen through electrolysis and the consumption of hydrogen through the use of fuel cells, as proposed in the frame of the hydrogen energy system. We revealed that the required 5000 kWh/year electricity and 1 m^3/year water are obtained by feasible hydrogen transportation.

Renewable energy-driven hydrogen generation is a favorable way. Renewable energy can be used to generate electricity that can be used to produce hydrogen through water electrolysis. Given the climatic conditions of Kazakhstan, the available renewable resource is solar power. If hydrogen energy becomes a conductor of energy, 1.34m^3/year of water per capita will be necessary as a source of hydrogen. The required energy amount to produce hydrogen for electricity consumption per capita is equal to the energy quantity made from hydrogen (if energy conversion efficiency is 100%). We consider the fuel cell with 50% efficiency for electricity and double power generation is required.

The energy consumption per capita in Kazakhstan is 5000 kWh/year, which can get by 7.44×10^4 mol /year of hydrogen. To produce this amount of hydrogen we need 1.34 m^3/year of water, 5.82×10^3 kWh of energy, which comes from 8.31×10^3 kWh /year of power consumption by electrolyzer, and 5.19×10^4 kWh/year of solar energy from solar cells with 34.6 m^2 of surface area.

Produced hydrogen will be stored in Ti-based hydrogen storage alloy because Kazakhstan has substantial resources of Ti, Cr, Fe, Mn, and their prices are lower than rare earth metals, which are used commonly for hydrogen storage material. Ti-based alloy will be prepared by MA, then transported by railway.

We assume the weight of transported hydrogen storage alloy per wagon is 5.4×10^4 kg with 1.5 wt% of hydrogen. The hydrogen capacity per wagon is 4.1×10^5 mol. If a regular train is composed of 50 wagons, 2.04×10^7 mol H_2 will be transported. If a train transports it 10 times per day, they transport 2.04×10^8 mol of H_2/day and 7.4×10^{10} mol /year. Approximately 3×10^7 kg/year of the alloy will be used.

We propose methods, such as the withdrawal of hydrogen from hydrogen storage alloy by a pump and the withdrawal of hydrogen storage alloy from the wagon to distribute hydrogen to fuel cell. A fuel cell system provides electricity and water on large, medium, and small scales depending on demand. Finally, more than 1 million people are provided with water and 0.4 million people with electricity by utilizing fuel cells.

The system is also capable of satisfying drinking water requirements, and society can become practically self-sufficient. In the future, the transportation possibilities of the fuel cell by train and utilization of fuel cells will be possible not only for large cities, but also for rural areas, and offers a significant opportunity for water supply. Transportation of hydrogen by storage alloys via railway allows the export of energy and water to neighboring countries. The water supply system considered here can be extended to other countries with water scarcity problems.

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CHAPTER IV: ACTIVATION CHARACTERISTIC OF Ti- BASED ALLOYS PREPARED BY MECHANICAL ALLOYING (MA) METHOD FOR MASS PRODUCTION

4.1. Activation of TiFe-based hydrogen storage alloys

The TiFe alloy can be considered one of the attractive hydride forming materials from the technological view. It is promising to use this industrial application because of several advantages such as moderate hydrogen absorption conditions, relatively high hydrogen storage capacity, and the abundance and low cost of its constituent elements Ti and Fe. TiFe is known to have a complicated activation process and high sensitivity. The activation process of TiFe is related to surface issues. The adsorbed hydrogen penetrates the surface before being dissolved in the material bulk. The limiting step of the activation mechanism is controlled by surface properties of the hydride forming material. Transition metals known as a clean surface promotes the molecular hydrogen gas's dissociation process and enhances the overall activation mechanism [1]. Necessary actions to perform when preparing to activate an intermetallic material are surface cleaning and removing the passivating oxides layers.

Generally, three different methods are usually used to perform the activation of TiFe alloy:

1) Thermal processes at temperatures over 673 K under argon, hydrogen, and/or vacuum atmosphere (heating and cooling cycles) [2-4];
2) Addition of transition metals (Pd, Ni and Mn) [5-8];
3) Mechanical processed by severe plastic deformation: mechanical milling [9-12].

Direct synthesis of TiFe alloys by ball milling would also be possible, but not easy, as the outcomes are sensitive to the milling process duration and intensity.

4.1.1 Activation of TiFe-based hydrogen storage alloys prepared by arc melting

Based on a literature survey, many publications discuss the activation process of TiFe or TiFe based alloys. TiFe related work started from 1970-1980 and was one of the popular topics for researchers because of the potential to realization in industrial scale.

For example, an arc melted TiFe sample has been activated by performing a 30 times pressure cycling (1×10^{-3} MPa to 4 MPa) at room temperature for 20 min. This process contributes to surface cleaning and promotes the reactivity of molecular hydrogen gas with hydride forming material [13].

Other researchers reported that TiFe is activated after heating at 670 K in a vacuum and annealing under 7 MPa of hydrogen pressure for 30 min [14].

TiFe air crushed samples are covered by 20–30 nm thick oxygen-rich film, which seems to prevent the molecular hydrogen to be adsorbed on the surface under ambient temperature. When the sample is exposed to high temperature, the surface area is modified by segregation and oxygen diffuses into bulk inside [15].

In this method, Ti diffuses to the surface and oxidizes, and the residual Fe formas a superparamagnetic residue that is responsible for molecular hydrogen dissociation [16].

Generally, as a result of many efforts to activate the TiFe alloy, the alloy needs an intensive initial activation process at high temperatures over 773 K under high hydrogen pressures over 6.5 MPa in 2 h.

4.1.2 Activation of TiFe-based hydrogen storage alloys prepared by MA

Hydrogenation properties of TiFe synthesized by mechanical alloying were different from those previously reported. The first plateau pressure was higher (0.5 MPa) than the value previously reported. However, the second plateau pressure was found to be much higher than the literature value (25 MPa) [17].

In the study of Oishi *et al.* the intermetallic TiFe alloy was successfully prepared by mechanical alloying of Ti and Fe metals. The formed nano-TiFe alloy with a mixture of nano and amorphous structures was found to have a very easy, activation behavior compared with a standard polycrystalline TiFe alloy [18].

In order to activate the TiFe alloy prepared by MA, the alloy needs an intensive initial activation process at temperatures lower 673 K under high hydrogen pressures over 2.7 MPa.

4.1.3 Activation of TiFeMn Hydrogen Storage Alloys Prepared by Arc Melting

thermo-chemical treatment has been performed on a $TiFe_{0.9}Mn_{0.1}$ hydride forming material. The sample is subjected to athermal treatment between 573 K and 673 K under high pressure of hydrogen gas atmosphere before any H_2 absorption attempt. This high-temperature range aims to promote the chemical reaction of dihydrogen on the surface oxides layers. This thermo-chemical treatment operating with conditions 24 h, 6 h, 2 h, 40 min, 15 min of treatment duration, the heating temperature of 673 K, 623 K, 3.2 MPa of hydrogen pressure in the reactor cell immediately activated. The important difference between the ordinary activation process is that the time - consuming alternative cycling is not required. This treatment affects only the particle surface but not the material bulk [19].

Mechanical processing by mechanical milling is also used. An experimental procedure to avoid activation is the milling of prepared alloy by arc melting under the hydrogen atmosphere. $TiFe_{0.9}Mn_{0.1}$ was milled for 0.5 h, 1.2 h, 5 h before activation. The effect of mechanical milling on microstructural and hydrogenation properties of $TiFe_{0.9}Mn_{0.1}$ has been investigated. Short-time mechanical milling is an efficient process to increase specific surface area and decrease both particle and crystallite size without leading to alloy composition variations, nor the formation of amorphous phases [20].

This is feasible under lab-scale conditions, however, it could be more difficult on an industrial scale. In any case, the milling atmosphere's oxygen content seems to have a great impact on the result of the process. A scaled-up milling process is applied for a short time to the TiFeMn alloy performed by industrial milling the process is utilized to ease the practical application of this room-temperature hydride by avoiding any subsequent thermal or mechanical process and the addition of transition metals for its activation [21].

TiFe and $TiFe_{0.85}Mn_{0.15}$ alloys can reach 1500 cycles and up to 30 thousand cycles, respectively, without almost any loss of capacity [22]. Moreover, in many cases, the activation was still proven to be necessary.

4.1.4. Effect of Addition Mn

The activation process of TiFe is related to surface issues and the absorbed hydrogen penetrates the surface before being dissolved in the bulk material. The limiting step of the activation mechanism is controlled by surface properties of the hydride forming material. Mn aggregates at the surface of the particles and assembles with Ti to form TiMn bond. TiMn reacts with hydrogen and forms entry points for diffusion to the core [23].

Mn is very effective in improving activation characteristics and enhancing the resistance against impure gasses [24].

We summarized heat treatment methods for TiFe and TiFeMn prepared by arc melting and MA (Table 9). MA method preparation and addition of Mn reduced the time of heat treatment and improved the pressure and the temperature.

Table 9 Heat treatment methods for activation of TiFe and TiFeMn prepared by arc melting and MA according to references and this research [16,18,20]

Heat treatment for Activation	Arc melting				Mechanical alloying			
	T (K)	P (MPa)	Time (min)	Ref.	T (K)	P (MPa)	Time (min)	Ref
TiFe	773 <	6.5	120	[16]	673 >	2.7	120	[18]
TiFeMn	673	3.2	40-120	[20]	673	2.7	15	(present research)

4.1.5 Effect of Pd/Al_2O3

The development of improved storage materials means that the activating processes necessary before use, or handling the material during loading and unloading cycles, are subjected to conditions that keep poisoning effects within tolerable limits. Since surface contamination cannot be avoided unless ultrahigh vacuum conditions are used, catalytic effects should play an essential role in the practical application. Research on hydriding film samples of titanium and other metals, and titanium films covered with overlayers of various metals, showed that the slow dissociation of H_2 molecules on film surfaces contaminated with O_2 is a critical partial reaction step. The remarkable enhancement in H_2 dissociation is observed if nickel, iron, or palladium acting as catalysts are present on the surface of oxidized titanium or storage materials [25].

The finding that impeded dissociation of H_2 on oxidized hydride formers is probably the main reason for the poisoning of storage materials initiated in a few experiments using mixtures of storage materials with palladium powder or palladium coated Al_2O_3. The dissociation of H_2 molecules should occur at the palladium particles and hydrogen atoms and then should reach the surface of oxidized storage material particles in contact with the catalyzer and enhance the reaction rate [25].

4.2. Experimental method of activation and sorption processes

In this study, we considered the activation process used TiFeMn , which is produced by the mechanical alloying method for mass production. This manufactured intermetallic powder is called "as received'" powder. Afterward, the "as received" powder is considered for the activation process and resistance of oxidation (with/without) catalyzer by using the Sievert type apparatus.

Moreover, the 'as received' powder is considered for Pressure-Composition-Temperature identification (*i.e.* thermodynamic characterization). PCT curve is measured at 295 K, 323 K, 338K. The change in the particle of the powders was examined by scanning electron microscopy (SEM, JCM-6000Plus NeoScopeTM). The phase identification of all of the prepared samples was carried out by X-ray diffraction (XRD) using Rigaku Mini Flex 600.

4.2.1. Effect of Mn to oxidation

A procedure for activation of the 'as received' powder consists of heat treatment. During this treatment, the sample is heated to a high temperature (from RT to 673 K) under a high pressure of hydrogen (2.7 MPa) atmosphere for 15 min. New hydrogen is introduced and cooled. Fig. 18 displays a schematic drawing illustrating the principle of the heat treatment.

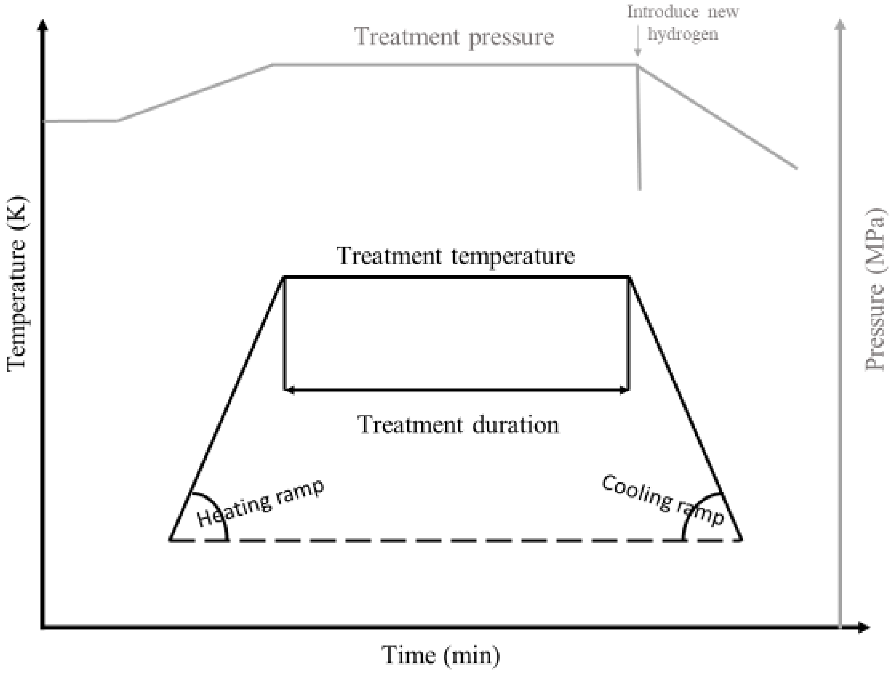

Fig.18 Schematic diagram of the performed heat treatment

Next, the treated sample is activated at RT, 1MPa, for approximately 15 min. The activation process is repeated 3 times (hydrogenation), then introduces air 0.05 MPa (oxidation 1) for 5 min. Then hydrogen was introduced (hydrogenation). Later air 0.1 MPa (oxidation 2) for 10 min.

4.2.2. Effect of Pd/Al_2O_3 to oxidation

10 wt% of Pd/Al_2O_3 was added to the 'as received' powder and mixed by shaking the reaction tube. the sample is heated to a high temperature (from RT to 673 K) under a

high pressure of hydrogen (2.7 MPa) atmosphere for 15 min (Fig.18). Afterward, the treated sample is activated at RT, 1 MPa for approximately 15 min. The activation process is repeated 3 times (hydrogenation), then introduces air 0.05 MPa (oxidation 1) for 5 min. Then hydrogen was introduced (hydrogenation). Later air 0.1 MPa (oxidation 2) for 10 min.

4.2.3. PCT at different temperature

A fresh ‘as received’ powder is considered for Pressure-Composition-Temperature identification (i.e. thermodynamic characterization). PCT curve is measured at 295 K, 323 K, 338 K. The change in the particle of the powders was examined by scanning electron microscopy (SEM, JCM-6000Plus NeoScopeTM). The phase identification of all of the prepared samples was carried out by X-ray diffraction (XRD) using Rigaku Mini Flex 600.

4.3. Results and discussion

4.3.1. Activation of TiFeMn

Fig. 19 demonstrates TiFeMn alloy’s activation results. Fig.19 to show that hydrogen absorption rate and amount of absorbed hydrogen are improved after activation 1, 2, 3. The absorbed hydrogen amount was obtained to be H/M= 0.89 after the activation 3.

The result of activation 4 after oxidation (0.05 MPa, 5min) is H/M= 0.02. However, when hydrogen was introduced again for activation 5, more than half hydrogen capacity, H/M= 0.52 of hydrogen absorbed. Here, we can see the effect of Mn. Mn has been found as enhancing the resistance against impure gasses and to be very effective in improving activation characteristics.

Afterward, 0.1 MPa of air was introduced for 10 min. Activation 6, 7 show that hydrogen did not absorb.

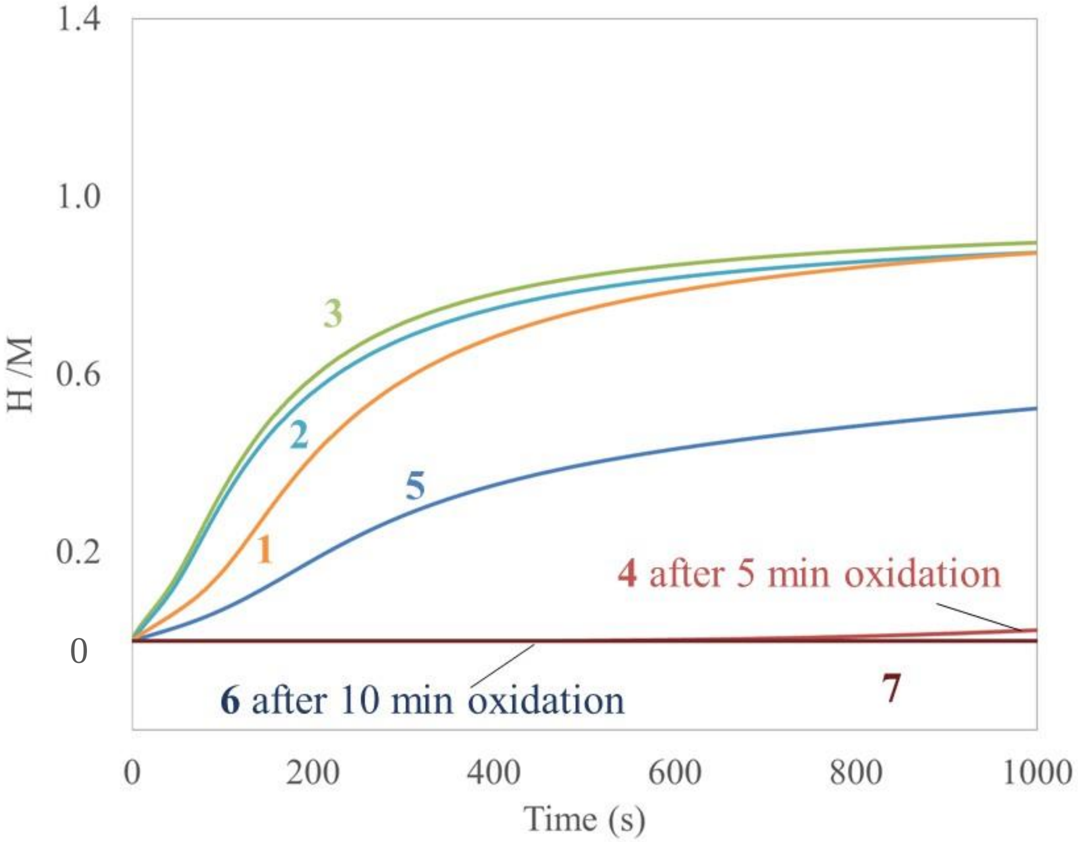

Fig. 19 Activation results of "as received" TiFeMn after oxidation

4.3.2. Activation of TiFeMn+Pd/Al_2O_3

Fig. 20 with TiFeMn+Pd/Al_2O_3 alloy's activation results summarized to show that hydrogen absorption rate and amount of absorbed hydrogen is improved after activation 1, 2, 3. After the activation 3, H/M= 1.19 of hydrogen was evaluated to be absorbed.

The result of activation 4 after oxidation (0.05 MPa, 5 min) corresponds to the concentration of H/M= 0.13. However, when hydrogen was introduced again for activation 5, almost half hydrogen capacity, H/M= 0.62 of hydrogen absorbed. Here, we can see the effect of Mn. Mn has been found as enhancing the resistance against impure gasses and to be very effective in improving activation characteristics.

Afterward, 0.1 MPa of air was introduced and kept for 10 min. Activation 6 shows that hydrogen did not absorb. When hydrogen is introduced (activation 7) again, H/M= 0.23 of hydrogen is absorbed.

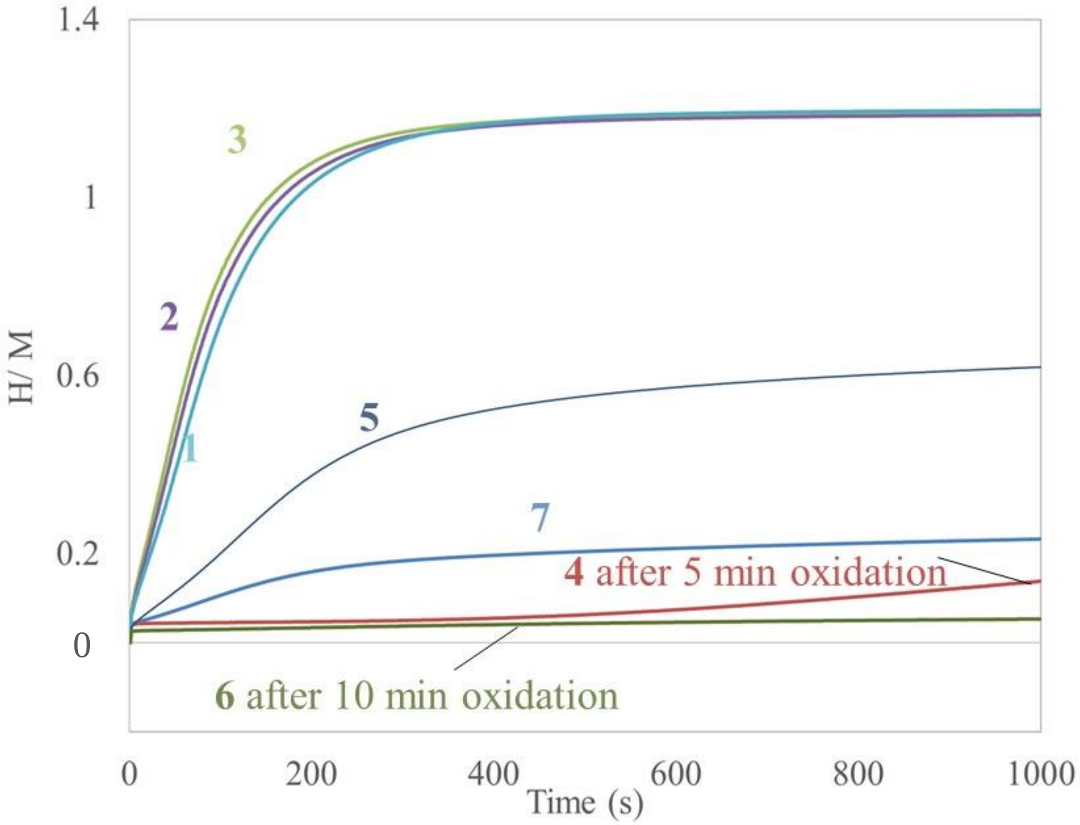

Fig. 20 Activation results of “as received” TiFeMn+Pd/Al_2O_3 after oxidation

Results of hydrogenation and oxidation are shown in Table 10, where we can see the effect of Pd/Al_2O_3 after heavy oxidization (0.1 MPa, 10 min). TiFeMn+ Pd/Al_2O_3 partially absorbed hydrogen then alloy without a catalyst.

It can be explained that the poisoning of the formation of hydride of metals and storage materials is, to a large extent, a problem of H_2 dissociation on the surface of poisoned material. Palladium can be used as dissociation catalysts if the overlay's thickness is large enough to act as a metallic coating or cluster. The activity of a palladium layer is recovering during exposure to hydrogen. Hydrogen atoms adsorbed after dissociation of the H_2 molecule on the surface of the catalysts can migrate or be spilled over to the surface of the poisoned alloy and drastically enhance the reaction rate [25].

Table 10 Hydrogenation and activation results for TiFeMn and TiFeMn+Pd/Al_2O_3

	Process	TiFeMn	TiFeMn+ Pd/Al_2O_3
1	Hydrogenation	○	○
2	Hydrogenation	○	○
3	Hydrogenation	○	○
4	Oxidation (0.05 MPa, 5min)	△	△
5	Hydrogenation	○	○
6	Oxidation (0.1 MPa, 10 min)	×	×
7	Hydrogenation	×	△

○ Absorption △ Partially absorption × Not absorption

4.3.3. PCT at different temperature

Next to powder activation a PCT curve at is carried out with increasing pressure doses from 0.5 to 15 bar is displayed in Fig. 21 and Fig. 22.

Hydrogen storage capacity decrease from H/ M=1.14 (295 K) to H/ M=0.05 (353 K), absorption plateau equilibrium pressure of plateau increase from 0.4 MPa (295 K) to 1.3 MPa (338 K), slightly sloping plateau is going upper, which show the infectivity of temperature effect to absorption and desorption. At 353 K, we can not see the plateau.

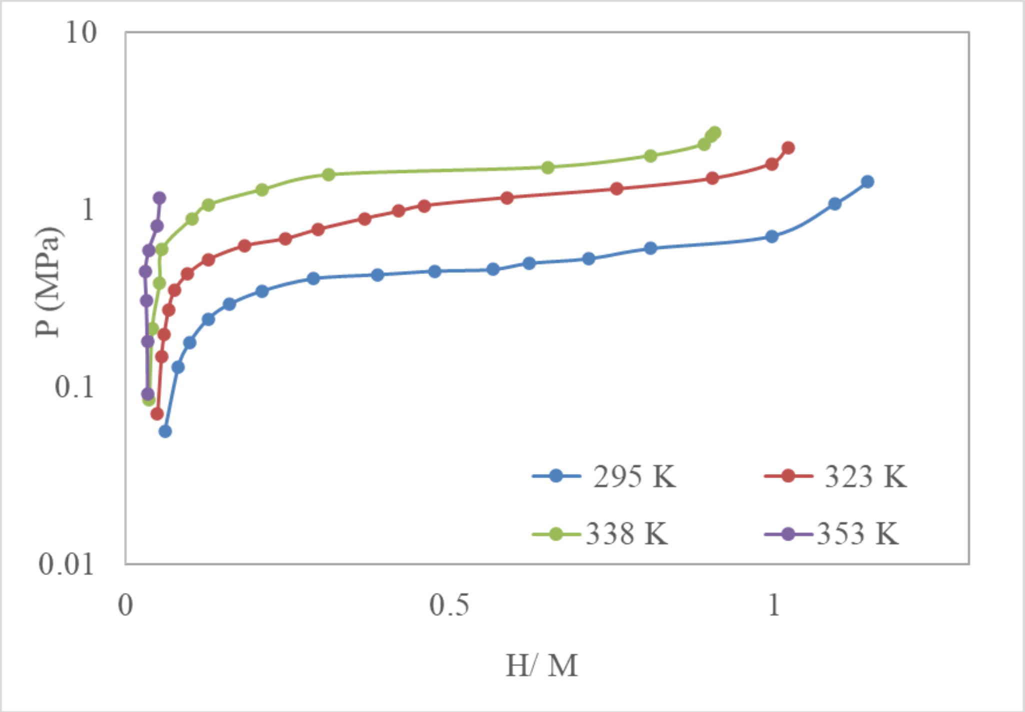

Fig. 21 PCT (absorption) of TiFeMn “as received” at 295 K, 323 K, 338 K, 353 K.

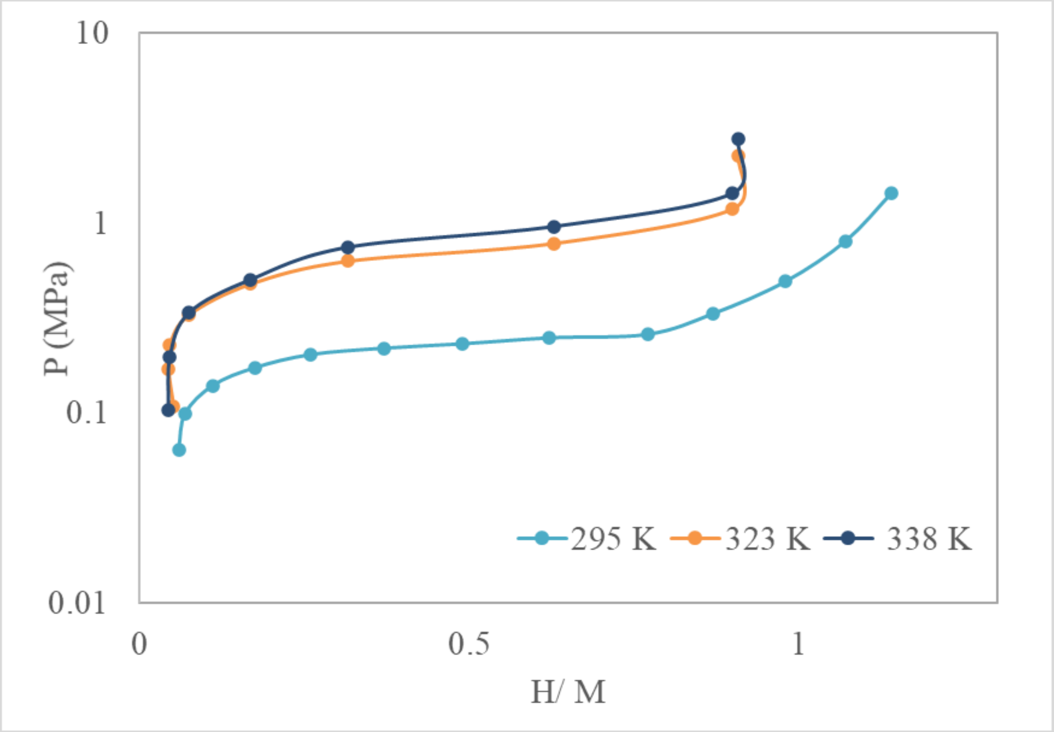

Fig. 22 PCT (desorption) of TiFeMn “as received” at 295 K, 323 K, 338 K, 353 K.

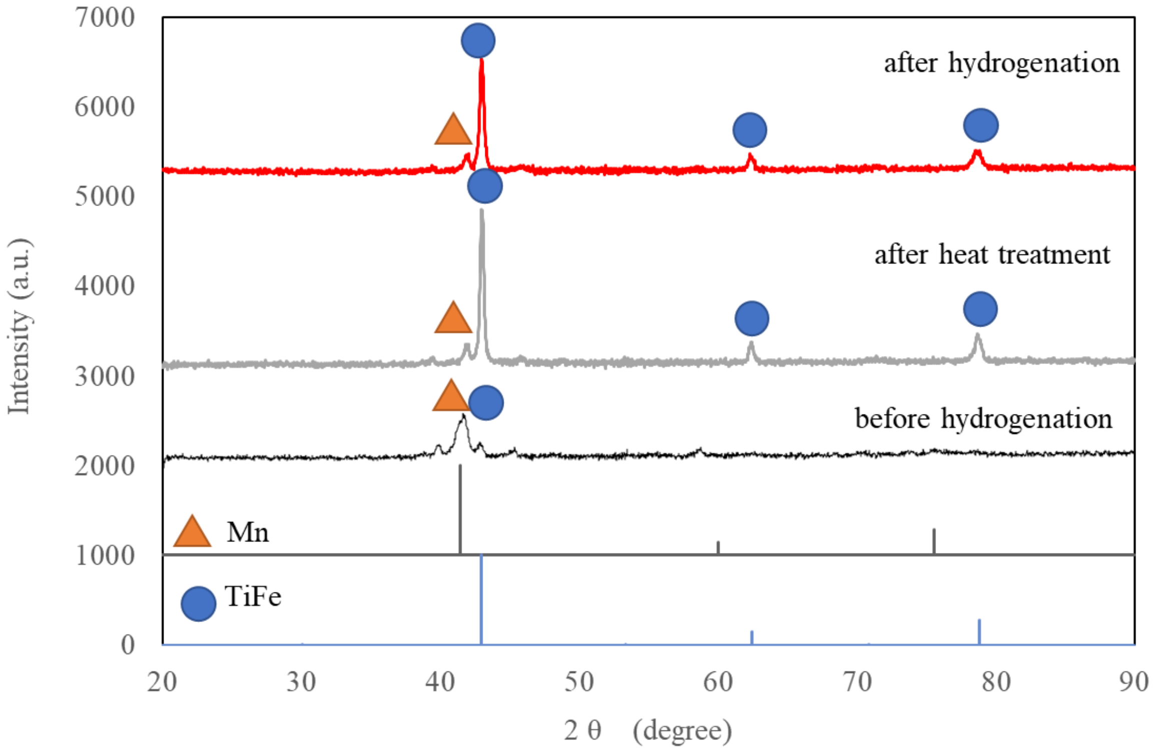

Fig. 23 XRD of sample TiFeMn "as received" before hydrogenation and heat treatment, after heat treatment and after hydrogenation.

Fig.23 shows XRD results for the as-received and before hydrogenation, after heat treatment, and after hydrogenation, respectively. Heat treatment shows the effect of annealing. A heat treatment alters the physical and sometimes chemical properties of a material to increase its ductility and reduce its hardness, making it more workable. It involves heating a material above its recrystallization temperature, maintaining a suitable temperature for an appropriate amount of time, and the subsequent cooling.

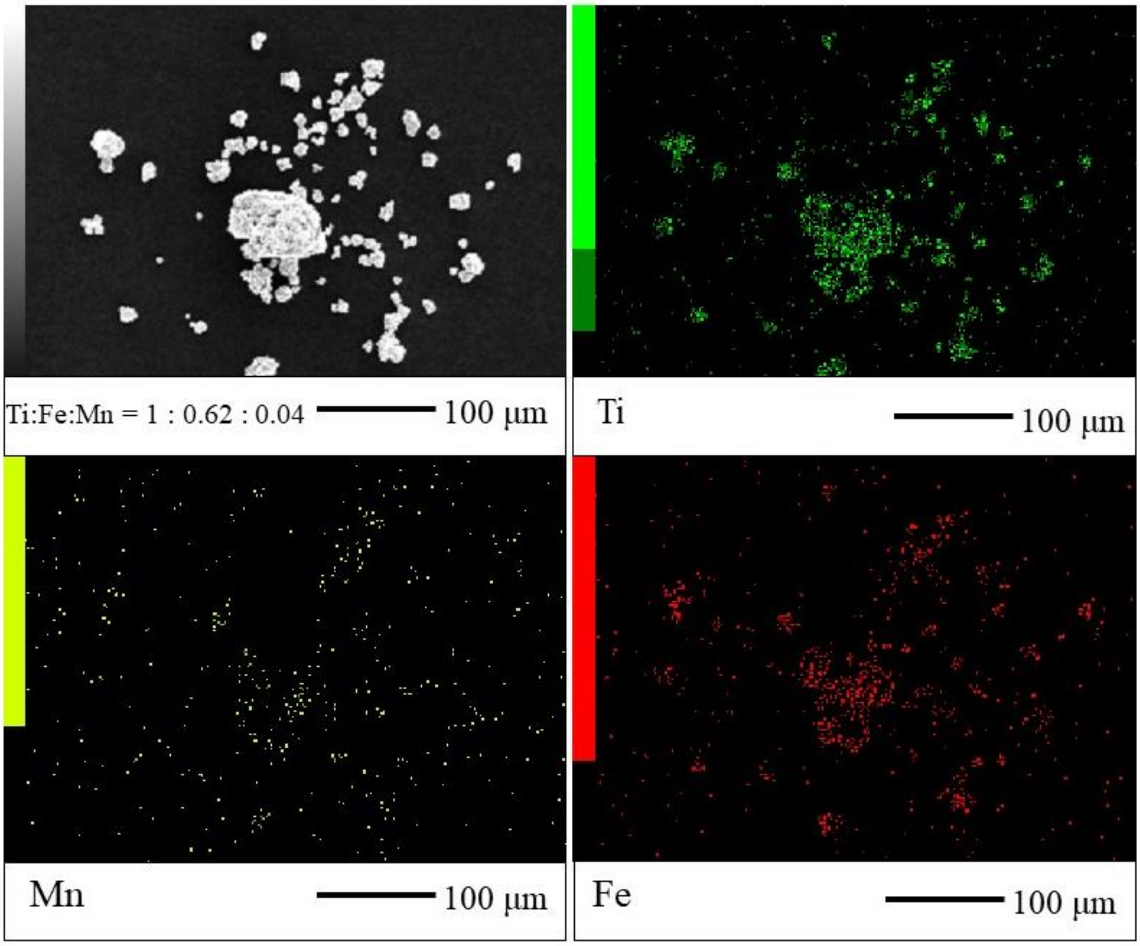

Fig. 24 SEM and EDS, mapping result TiFeMn “as received” before hydrogenation and heat treatment

After heat treatment mainly exhibit the characteristics reflections coming from TiFe alloy. The presence of Mn is not evident in the diffractograms, owing to its small amounts from the result of EDS analysis and mapping. EDS measurements are made to confirm the chemical composition of powder, showing the composition rate of Ti:Fe:Mn = 1 : 0.62 : 0.04 (Fig. 24).

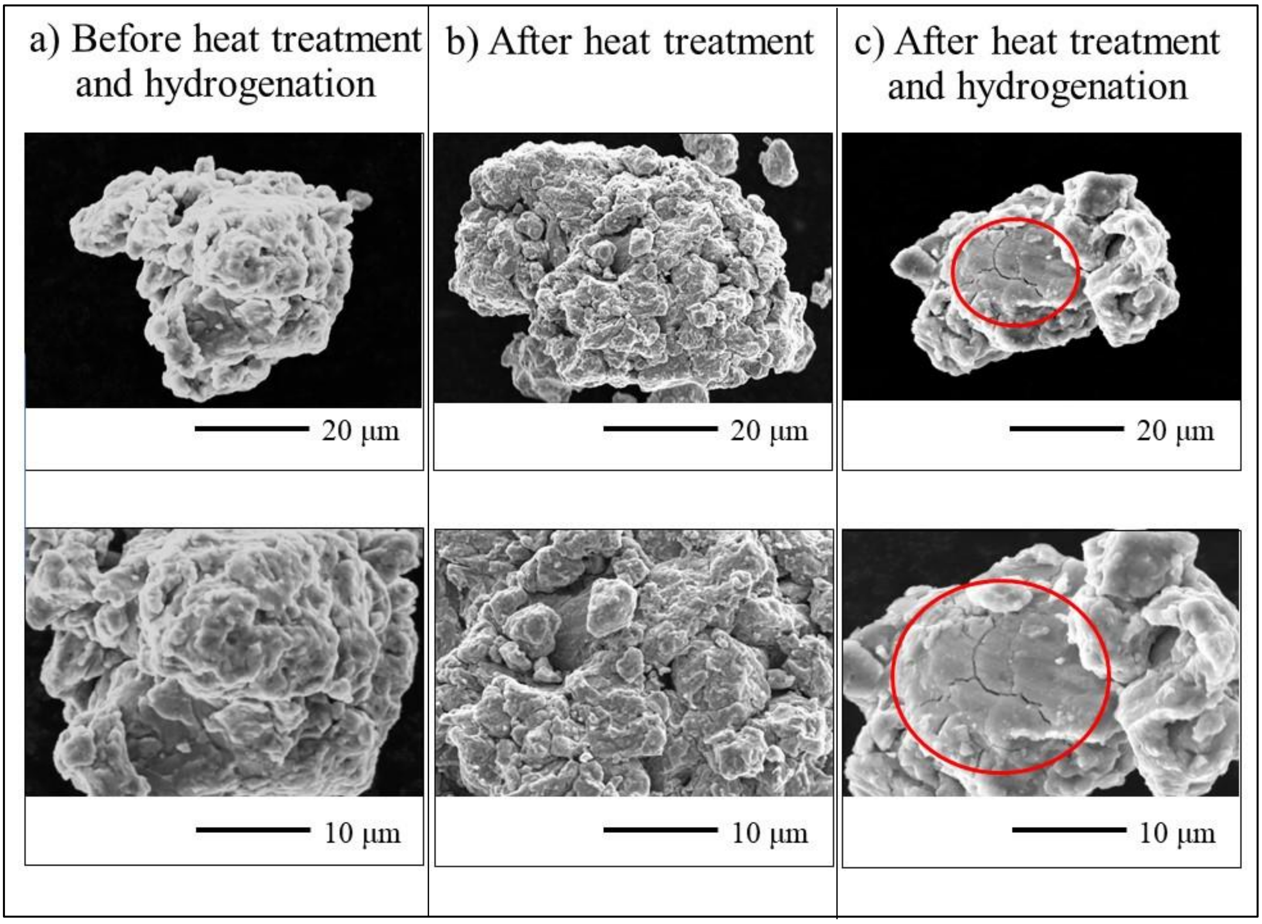

Fig. 25 SEM of TiFeMn “as received” a) before hydrogenation and heat treatment, b) after heat treatment, c) after heat treatment and hydrogenation

Fig. 25 shows the samples a) before heat treatment and hydrogenation, b) after heat treatment (673 K under hydrogen pressures over 3.2 MPa in 15 min), but not activated, c) after heat treatment in the same condition and activated. Fig. 25 shows a comparison between their SEM images, the difference in particle size, and change in surface.

The form of all samples has a swelling/ shrinkage on the surface, which is a result of MA. In the case of a) and b) particle size increased, because after heat treatment the powder is integrated. This increase of the specific surface area of intermetallic particles will have a positive effect on the activation. The high gas pressure of this treatment leads to the formation of a solid solution of the hydrogen gas and thereafter to possible embrittlement at the grain boundaries or the microstructural defects when the pressure suddenly falls leading to the creation of new exchange surfaces for hydriding/ dehydriding. Probably, reduction of the oxides layers begins with alternative cycling then continues during the incubation time and lasts much longer due to the lower temperature. However, the surface did not defect, which shows heat treatment did not have a thermo-chemical effect [20].

To compare with a) b), particle size in c) is reduced to 20 nm. Hence, during hydrogen absorption and desorption lead to enhance the powder embrittlement. SEM images c) after hydrogenation exhibit the creation of cracks at the surface of the particles which act as gates for a better diffusion of the hydrogen inside the material.

4.4. Summary of chapter

The TiFe alloy can be considered one of the attractive hydride forming materials from the technological view. It is promising to use this industrial application because of several advantages such as moderate hydrogen absorption conditions, relatively high hydrogen storage capacity, and the abundance and low cost of its constituent elements Ti and Fe. TiFe is known to have a complicated activation process and high sensitivity. In order to activate the TiFe alloy, the alloy needs an intensive initial activation process at high temperatures over 773 K under high hydrogen pressures over 6.5MPa in 2 h. In the case of TiFe alloy prepared by MA, the alloy needs an intensive initial activation process at temperatures lower 673 K under hydrogen pressures over 2.7 MPa.

When Mn is added to TiFe, TiFeMn is prepared by arc melting needs at temperature 673 K under hydrogen pressures over 3.2 MPa in 15 min. This chapter considered characteristic of TiFeMn prepared by MA method for mass production. The activation process needs 673 K under hydrogen pressures over 2.7 MPa in 15 min. As a result pressure, temperature, and time are decreased compared with TiFe prepared by arc melting, mechanical alloying, and TiFeMn, which are prepared by arc melting method.

However, an alloy prepared by MA after hydrogenation is not resistant to oxidation, like casted alloy. It needs to be recovered. Hence a catalyzer such as Pd/Al_2O_3 affects oxidation. Experiment results show after 10 min of 0.1 MPa oxidation, TiFeMn+PdAl_2O_3 absorbed hydrogen, while TiFeMn without catalyzer did not absorb hydrogen.

Moreover, PCT at different temperatures was obtained. As results show, by increasing temperature TiFeMn alloy characteristics are decreasing. For example, Hydrogen storage capacity decreases from H/ M=1.14 (295 K) to H/ M=0.05 (353 K), absorption plateau equilibrium pressure of plateau increases from 0.4 MPa (295 K) to 0.13 MPa (338 K), slightly sloping plateau is going up, which shows the infectivity of temperature effect to absorption and desorption.

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CHAPTER V: SELECTION of MATERIALS for PREPARING Ti-based ALLOY (Ti or TiH_2) by MECHANICAL ALLOYING (MA)

5.1. Ti-based alloys

Hydrogen storage alloys have attracted significant attention because they are safe and efficient media for transporting hydrogen energy. Multicomponent alloys of hydrogen storage compounds (AB, AB_2, AB_5, and A_2B-type) have been broadly studied in the last 3–4 decades. Subsequently, the electrodes of AB_5 ($LaNi_5$)- and AB_2 (ZrV_2)-type alloys have already been implemented in rechargeable nickel-metal hydride (Ni/MH) batteries. The representative alloys among the most promising hydrogen storage materials are titanium-based because of their storage property and cost-effectiveness [1]. Currently, practically useful hydrogen storage alloys are made from rare earth metals, which are very expensive. Ti-based alloys are mentioned among the most promising materials [2].

In general, in the production of Ti-based alloys by the MA method, TiH was sometimes used as a starting material because it was relatively inexpensive and easily pulverized, but compared with using metallic Ti such as titanium sponge. The effect on alloy production when the milling conditions were constant was not clarified. Therefore, in this study, we investigated the alloy characteristics obtained when Ti and TiH were used as the starting materials.

5.1.1. $TiCr_2$-based alloys

Among the various types of metal hydrides, AB_2 type Ti-Cr-based alloys are the most promising candidates due to their relatively high desorption pressure plateaus and moderate hydrogen storage capacities, fast kinetics, and easy activation. However, they are still far from the targets for high-pressure alloys for hybrid systems due to their relatively high hydrogen desorption pressures and low capacities. For example, $TiCr_2$ has a too high absorption plateau of 100 MPa even at a low temperature of 195 K, which is much higher than the maximum working pressure of a hybrid tank. Alloying with other elements is one of the most effective ways to adjust the formation enthalpy and cell volume of metal hydrides, allowing considerable influence over the hydrogen absorption/desorption pressure and capacity [3]. The ternary intermetallic TiCrMn is partially manganese substituted derivative of the C14 Laves phase $TiCr_2$. The C14 Laves phase TiCrMn has attracted much attention because of the outstanding physical and chemical properties, especially for its potential application as a hydrogen storage material.

Due to this partial substitution of the Cr by Mn, the host (hydrogen-free) intermetallic and its corresponding hydride phases are also altered [4].

5.1.2. TiFe- based alloys

TiFe-based alloys are used. Its use and application have been studied because of its price advantage. Since initial activation is difficult compared to other alloys [5], the activation mechanism has been investigated, and the effect of changes in surface structure due to oxidation and the effect of Ti-rich layers [6-9]. Many researchers tried to find methods to solve the problem of activation, such as the addition of a small amount of Mn, [10-11], the addition of sulfur [12], or the amorphization of surface structure [13].

Generally, alloy production methods such as the high-frequency induction melting method and arc melting method are used in alloys, but when a component having a high vapor pressure such as Mn is contained, composition control is difficult and a large amount is used. In the case of manufacturing, a large-capacity electric power facility is required.

Since the initial activation tends to be improved by adding Mn to the TiFe-based alloy, the TiFeMn-based alloy to which Mn is added is prepared. When Mn addition is prepared by the melting method, it is challenging to adjust Mn's component with high vapor pressure. Therefore, alloy production by the MA method is considered, but when MA is used for this alloy system, if it is performed in an Ar atmosphere and the pot is made of stainless steel, Mn will react with the pot's wall. Composition control becomes difficult. In that case, it has been reported that the reaction between Mn and the pot wall can be suppressed by using dehydrated hexane [14].

5.1.3 Mechanical alloying by ball milling methods

In recent years, mechanical alloying (MA) by ball milling (BM) has been used as a manufacturing method that includes features such as controlling the composition of hydrogen storage alloys and facilitating initial activation by intentionally reducing the crystallinity near the surface [15].

MA method mixes different elements by repeating mechanical impact and rolling to realize ultrafine dispersion or alloying. Generally, this is a way to use a ball milling.

The most remarkable feature is that alloys can be produced without melting metals. In 1970, the MA method was proposed by International Nickel Corporation (INCO) as a method for producing particle-dispersion-strengthened nickel-based superalloy powder [15].

The ball mill is the most commonly used means for performing the MA method, which has been used to develop various structural and functional materials. A ball mill is an apparatus initially designed for crushing. It is a method of crushing a sample by enclosing a hardball and an example in a container and rotating and vibrating the pot. Three ball mills are known: rolling type, planet type, and vibration type [16].

The MA method is expected to exhibit the following effects, such as:

(1) More acceptable structure and complex structure

(2) Dispersion of fine structure

(3) Alloying

(4) The appearance of thermodynamic nonequilibrium phase

(5) Amorphization

Obtaining hydrogen storage alloys of TiFe systems, the mechanical alloying process has been more frequently used because of its various scalability and the possibility of using elements of different vapor pressures. Usually, ball milling is carried out under inert gas or using hexane dehydrated, avoiding powder oxidation during mixing. Hydride powder is preferably used because hydride is more brittle and useful for keeping a reducing environment.

MA can synthesize various nonequilibrium alloys, so it has been widely applied to modify a hydrogen storage alloy [17]. Compared with the arc melting method, the MA method enables synthesizing at low power for a long time. Moreover, since at the same vapor pressure 133 Pa, the temperature of Mn (1522 K) is lower than the other metals Cr (1968 K), Fe (2063 K), Ti (2464 K), it can be prepared by MA at room temperature [18]. Therefore, MA is an easy way to prepare hydrogen storage alloy because it does not need special equipment.

5.2. Experimental method

Metal powders of 99% purity were mixed with an atomic ratio of 1 : 1 : 1.

The MA rotation speed was constant at 300 rpm by planetary ball-mill (Retsch, Planetary Ball Mill PM 100), and the MA time was 100 h in dry and wet conditions. Also, in order to see the effect of MA time, the alloy state after 10 h, 20 h, 50 h and 100 h were analyzed. The powder sample is sealed and opened in the pot in the glove box in the Ar atmosphere. When the pot is opened, the powder sample lies in the Ar atmosphere for a particular time not to cause rapid oxidation, and the surface is exposed. After it becomes stable, it was taken out into the atmosphere. Titanium sponge and Ti hydride were used as the metal Ti, and titanium sponge, having an initial particle size of about 1 mm, was pulverized in advance with MA for 10 hours to make it almost the same as other sample powders. After crushing, it was taken out into the atmosphere and left in the air from 1 day to 1 month. Fig. 26 shows an SEM image of the starting material before MA. Since Ti hydride is brittle and easily atomized, it can be seen that it is more refined than Ti powder in the state before MA. Further, the obtained sample was subjected to XRD (X-Ray Diffraction) analysis by Rigaku MiniFlex with Cu target and SEM/ EDS (Scanning Electron Microscopy/ Energy-dispersive X-ray spectroscopy) analysis by JCM-6000Plus NeoScopeTM.

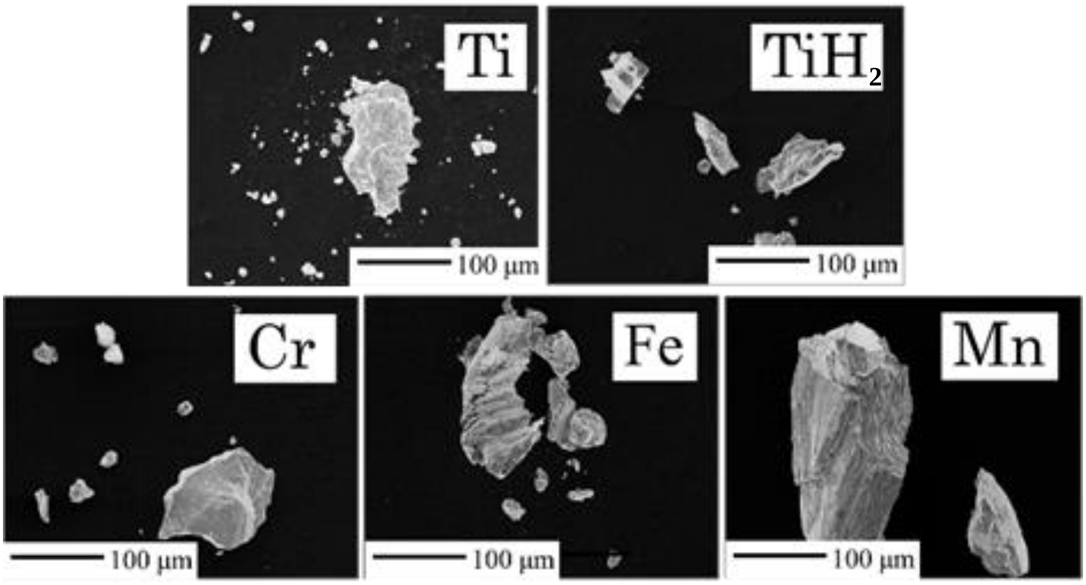

Fig. 26 SEM images of powder sample before MA

5.2.1. Effect of preparation TiCrMn in dry condition

For the MA in dry condition, a mixture of the powder was sealed with stainless steel balls in a stainless steel pot. Alternatively, ceramic balls and a ceramic pot were also employed to compare the results with stainless steel balls and pot. In both MA treatments, MA was rotated at a speed of 300 rpm for 50 h. The ration of the ball to the sample in weight is 1 : 10. Milling balls with a diameter of 8 mm were used. In addition, the composition analysis of prepared powders was performed.

5.2.2. Effect of preparation TiCrMn in wet condition at different MA time

For the MA treatment in wet conditions, the pot was filled with hexane (super dehydrated) as a dispersion medium up to 2/3 of the pot's volume made of stainless steel and ball-milled using stainless steel balls.

TiCrMn-based alloys, powder samples were prepared with Ti, Cr and Mn and TiH_2, Cr, Mn with target composition 1: 1: 1. MA time was 10 h, 20 h, 50 h, and 100 h. In addition, XRD analysis and SEM / EDS analysis were performed.

5.2.3. Effect of TiH_2 on the preparation of Ti-based alloy

TiFeMn- based alloy, powder samples were prepared Ti, Fe, Mn and TiH_2, Fe, Mn with the same ratios as previous samples. MA time is 100h. The obtained sample was subjected to XRD analysis and SEM / EDS analysis.

5.3. Results and discussion

5.3.1. Preparation of TiCrMn alloy in dry condition

The results of the EDS analysis on powders obtained by dry MA conditions using stainless steel and ceramic pots are shown (Table 11). In the case of the dry MA treatment in a stainless steel pot, Mn concentration in the sample powders after the MA showed much lower concentration than expected. This was caused by significant fixation of Mn on the inner wall of the pot, as confirmed by eyesight after the MA treatment. The same MA treatment using a ceramic pot also resulted in fixation and caused large subtraction of the composition from the nominal composition of Ti : Cr : Mn = 1 : 1 : 1, as shown in Table 9. Moreover, significant amounts of Al and O were detected, reaching 16.2 at. % and 10.4 at%, respectively. This contamination of the sample powders by Al and O originates from the ceramic pot and balls, which means fine particles of Al_xO_y were mixed with powders of Ti, Cr, and Mn. The results suggested that the fixation cannot be avoided unless a dispersion medium is used for the MA. In the next section, the results of the MA in wet conditions are shown.

Table 11 Result of EDS analysis of samples milled by dry type

Element	(at. %)				
	Ti	Cr	Mn	Al	O
MA-treated in stainless steel pot	49.1	40.1	10.8	-	-
MA-treated in ceramic pot	14.3	6.30	29.4	13.8	36.2

5.3.2. Preparation of TiCrMn alloy in wet condition at different MA time

The particle size of milled powders decreased with increasing MA time, while the morphology did not show a clear difference as shown for Ti-Cr-Mn (Fig. 27). For each powder sample, EDS analysis was carried out at different regions of the SEM image to confirm compositional homogeneity. The respective zones, a, b, and c are marked in each image shown in Fig. 27. The results of EDS are shown in Table 12. Ti, Cr, and Mn powers were mixed to the target amount in an atomic ratio of 1 : 1 : 1. Milling for 10 h and 20 h resulted in the composition ratio of Ti : Cr : Mn = 1.00 : 0.38 : 0.66 and 1.00 : 1.44 : 1.84 (zone a), respectively. The composition of the samples was not identical to the target values in an atomic ratio of 1 : 1 : 1. At prolonged milling for 50 h, the composition of all surface showed 1.00 : 0.97 : 0.83 (zone a), which is close to the nominal composition. However, regarding the results of b and c zones focused on grains, the composition was different, suggesting that the MA is still insufficient. MA treatment for 100 h, the longest milling time in this study, marked the composition of 1.00 : 1.01 : 1.09 ,1.00 : 1.17 : 1.01 and 1.00 : 1.08 : 1.18 at zone a, zone b, and zone c, respectively. Particle analysis indicates that the compositional difference between average scale and individual particle decreased as the milling time increased. Even longer MA treatment could completely homogenize the composition [19].

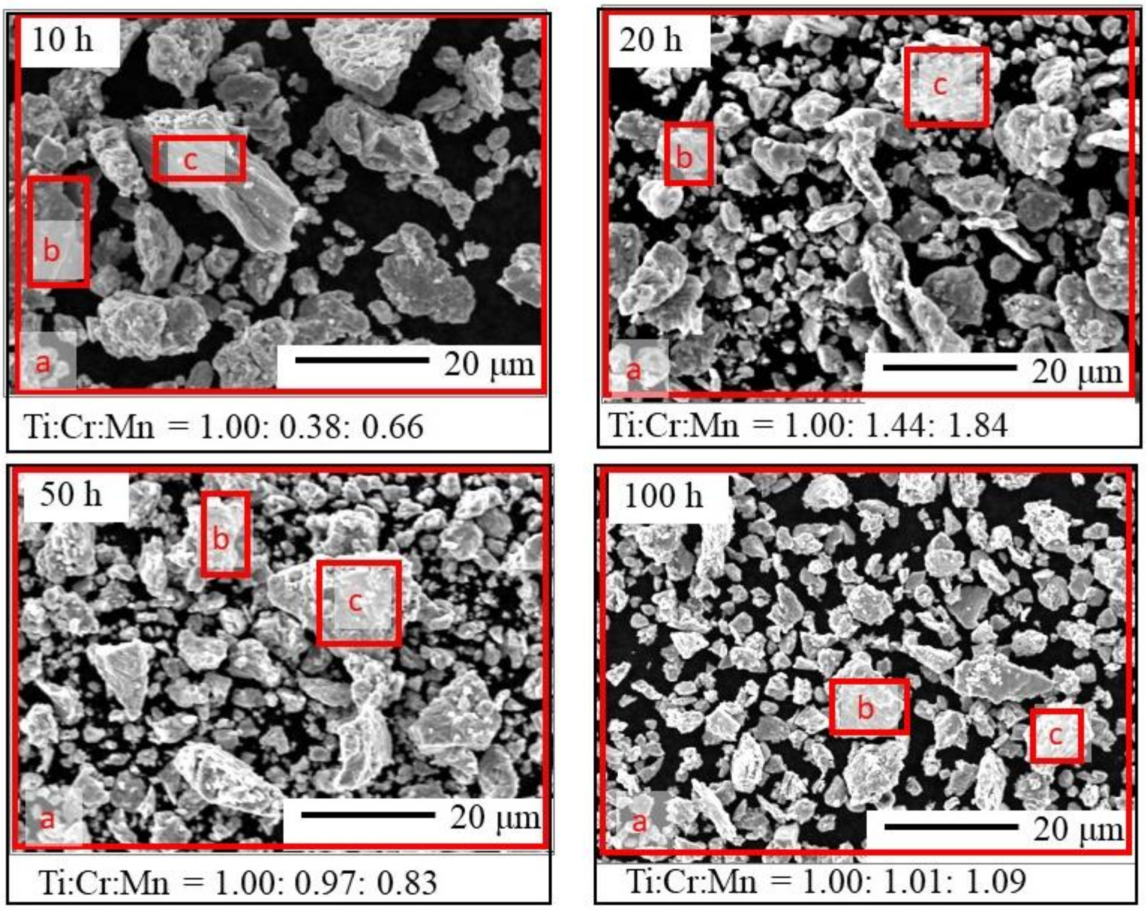

Fig. 27 SEM images show a different particle size at different milling time and region of EDS analysis with a, b, c zones for Ti-Cr-Mn [19]

Table 12 Result of EDS analysis of Ti-Cr-Mn as milled

by wet type for a different period

Milling Time		10 h	20 h	50 h	100 h
Zone	Element	(at %)	(at %)	(at %)	(at %)
a	Ti	48.8	23.3	35.5	32.2
	Cr	18.7	33.6	34.7	32.6
	Mn	32.5	43.0	29.8	35.2
b	Ti	50.7	16.7	37.9	31.3
	Cr	16.2	66.7	30.1	36.8
	Mn	33.1	16.6	32.0	31.9
c	Ti	50.1	21.3	30.6	32.2
	Cr	19.9	46.9	27.2	29.7
	Mn	30.0	31.8	42.2	38.1

Fig. 28 shows the XRD spectra of the Ti-Cr-Mn mixtures mechanically alloyed with different milling times. After a milling time of 10 h, the peaks of the TiCrMn phase were found. But, Ti, Cr, and Mn peaks are still present. A strong Ti peak of $2\theta = 40.2^\circ$ was evident. Milling for 20 h leads to a reduction of the Ti peak. After 50 h of milling, the XRD pattern was dominated by peaks from the TiCrMn phase. The height of the Ti, Cr, and Mn peaks became the background level. After the MA was milled for 100 h, the XRD result suggests almost a single phase of TiCrMn. This is consistent with the EDS results, which focused on a mechanical composition control for the mass production of hydrogen storage alloys. Using the process of ball milling by wet type with different times obtained different morphology and microstructure. The evolution of the particle size was determined. The alloy obtained from 100 h of milling had the smallest average particle size and the closest composition to the target atomic ratio of elements.

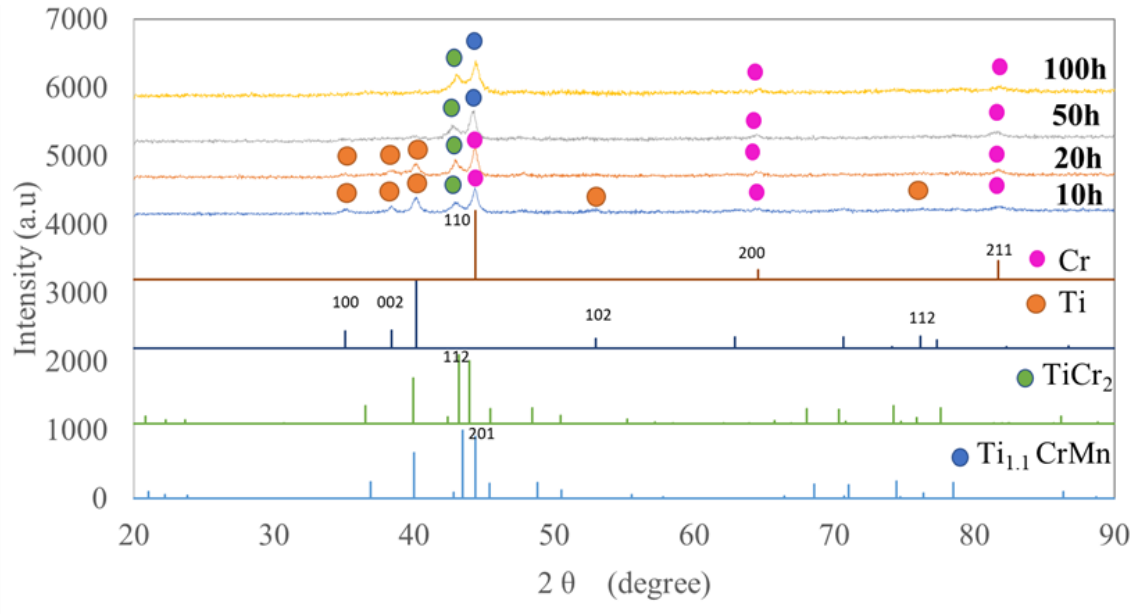

Fig. 28 XRD spectra of samples of Ti-Cr-Mn after 10 h, 20 h, 50 h and 100 h of MA under atmosphere of hexane super dehydrated

The particle size of milled powders decreased with increasing MA time, while the morphology did not show a clear difference as shown for TiCrMn prepared by using of TiH_2 (Fig. 29). For each powder sample, EDS analysis was carried out at different regions of the SEM image to confirm compositional homogeneity with the respective zones, a, b, and c. The results of EDS are shown in Table 11. TiH_2, Cr, and Mn powers were mixed to the target amount in an atomic ratio of 1 : 1 : 1. Milling for 10 h and 20 h resulted in the composition ratio of Ti(TiH_2) : Cr : Mn = 1.00 : 0.42 : 0.62 (zone a) and 1.00 : 0.76 : 0.63 (zone a), respectively. The composition of the samples was not identical to the target values in an atomic ratio of 1 : 1 : 1. At prolonged milling for 50 h, the composition showed 1.00 : 0.83: 0.75 (zone a), which is relatively closer to the nominal composition. However, regarding the results of b and c zones focused on grains, the composition was different, suggesting that the MA is still insufficient (Table 12). MA treatment for 100 h, the longest milling time in this study, marked the composition of 1.00 : 0.96 : 0.91, 1.00 : 0.99 : 0.97 and 1.00 : 0.96 : 0.92 at zone a, zone b, and zone c respectively.

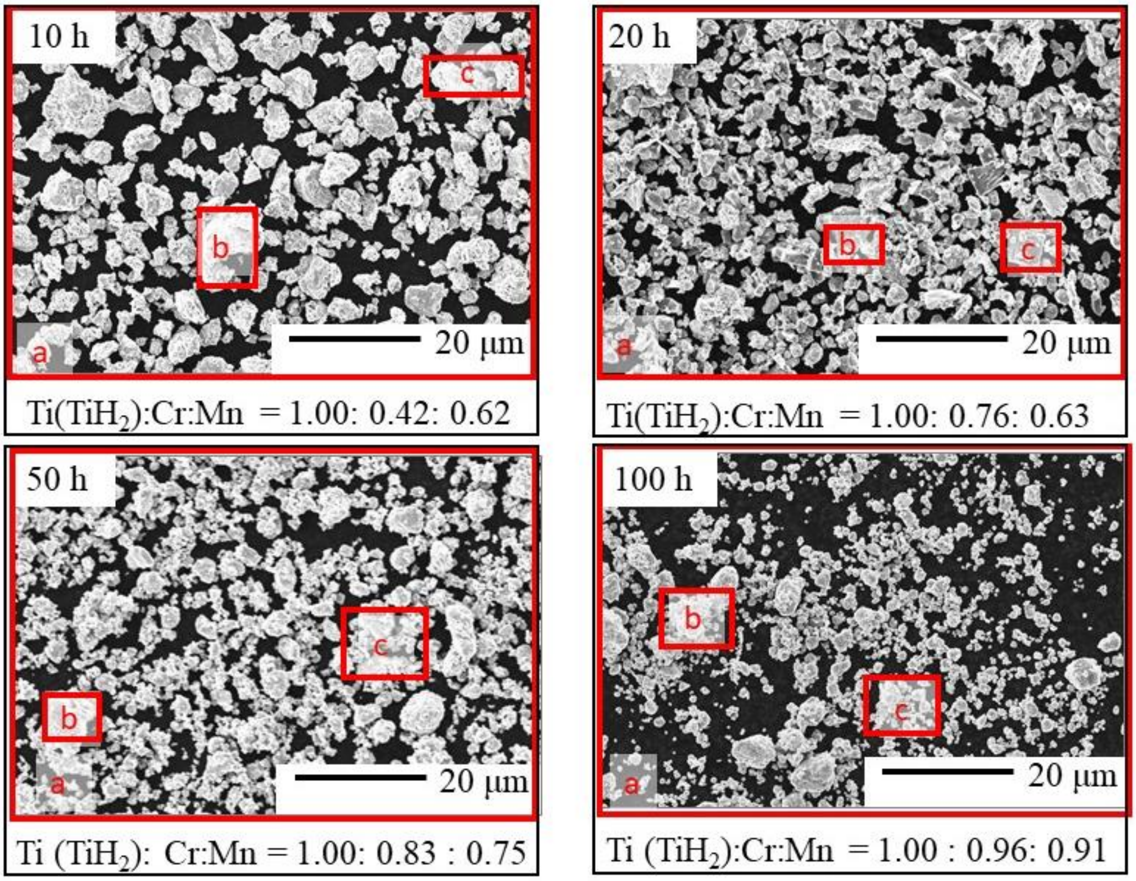

Fig. 29 SEM images show a different particle size at different milling time and region of EDS analysis with a, b, c zones for TiH_2-Cr-Mn

Table. 12 Result of EDS analysis of TiH_2-Cr-Mn as milled by wet type for a different period.

Milling Time		10 h	20 h	50 h	100 h
Zone	Element	(at %)	(at %)	(at %)	(at %)
a	Ti	48.2	41.7	38.5	34.7
	Cr	20.7	31.8	32.3	33.5
	Mn	30.1	26.5	29.2	31.8
b	Ti	40.7	37.2	39.6	33.8
	Cr	46.3	20.0	31.4	33.4
	Mn	13.0	42.8	29.0	32.8
c	Ti	40.1	40.6	36.1	34.6
	Cr	49.1	38.2	35.4	33.4
	Mn	10.8	21.2	28.5	32.0

Fig. 30 shows the XRD patterns of the TiH_2-Cr-Mn mixtures mechanically alloyed with different milling times.

When Ti or TiH_2 is used, we see that the TiCrMn phase is formed after 50 h. However, when TiH_2 was used, the TiH_2 phase could be confirmed even after 50 h, and a slight TiH_2 phase was observed even after 100 h, and the alloying did not proceed sufficiently under the same MA conditions.

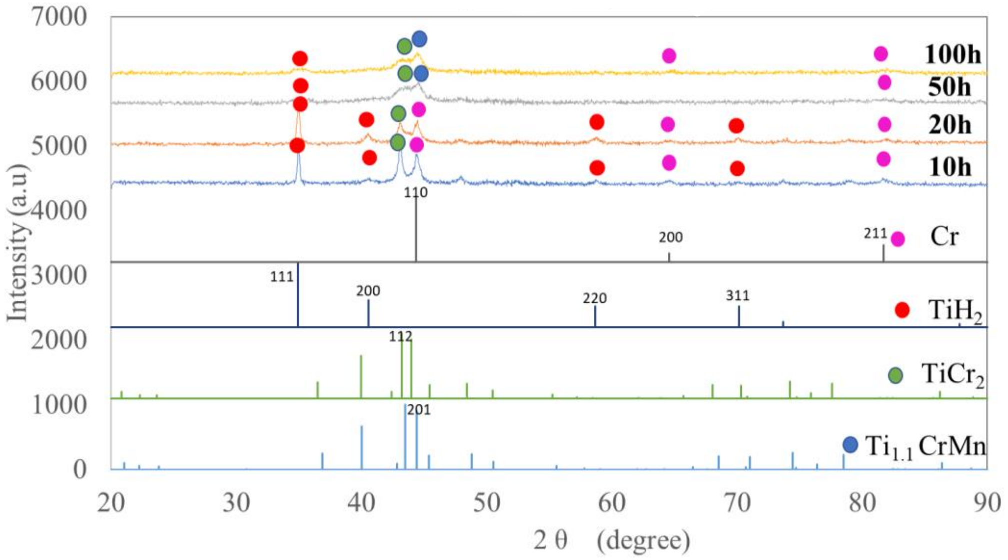

Fig. 30 XRD of samples of TiH_2-Cr-Mn, after 10, 20, 50 and 100h of MA under atmosphere of hexane super dehydrated

Fig. 29 and Fig. 30 show that when TiH_2 is used, pulverization has already progressed at 20 h as compared with the case where Ti is used. After 100 h, the brittleness of TiH_2 confirms that the particle size is significantly smaller, but the XRD results show that alloying has not progressed.

According to the composition analysis result by EDS, after 100 h, the mixing ratio is almost equal to the target composition (Fig. 29). However, at 10 h to 50 h, the particle distribution is not uniform in the observation area, and it is observed as a composition deviation.

On other hand, when the metal Ti is used, it can be seen that after 50 h (Fig. 30), all the phases are $TiCr_2$ or TiCrMn. In $TiCr_2$ [20-21] or $TiMn_2$ [22-24], the stable phase at low temperature is the C14 Laves phase, but it is known that the bcc phase can be obtained by applying excessive energy by ball milling. In this research, the obtained XRD results show the same tendency as in the previous works (Fig. 30).

Interestingly, when TiH_2 was used, the peak of $TiCr_2$ was larger than that of the TiCrMn phase after 10 h, and this tendency was observed even after 20 h. The TiH_2 phase coexists, and it can be seen that TiH_2 and $TiCr_2$ disappear and change to the TiCrMn phase (Fig. 30).

In the TiCr phase, it is expected that TiH_2 can be alloyed relatively quickly even if TiH_2 is used as a starting material, and it is presumed that after alloying TiH_2 and Cr, it reacts with Mn while leaving TiH_2, which is difficult to alloy. When Cr or Mn is added to TiFe, it has been reported that Mn hardens the crystal compared to Cr [25], and it is speculated that the mechanical properties affect.

On the other hand, when Ti is used, Ti, Cr, and Mn are alloyed simultaneously, and the size of the peak after 100 h shows that the growth is faster than when TiH_2 is used. In order to obtain the TiCrMn phase in a shorter time, it is possible to obtain Ti faster than TiH_2.

5.3.3. Preparation of TiFeMn alloy in wet condition and effect of TiH_2

Fig. 31 shows SEM observation results of an attempt to produce a TiFeMn-based alloy by the MA with Ti and TiH_2 as starting materials. The composition is shown as calculated by EDS analysis. The sample powder's size is crushed from several μm to about 20 μm, but it can be seen that the sample using TiH_2 is particularly smaller.

The fine powder in the SEM image is TiH_2 itself, and TiH_2 is brittle and easily pulverized in MA. It has a strong tendency to be crushed without being alloyed, and it can be seen that it tends to be difficult to alloy.

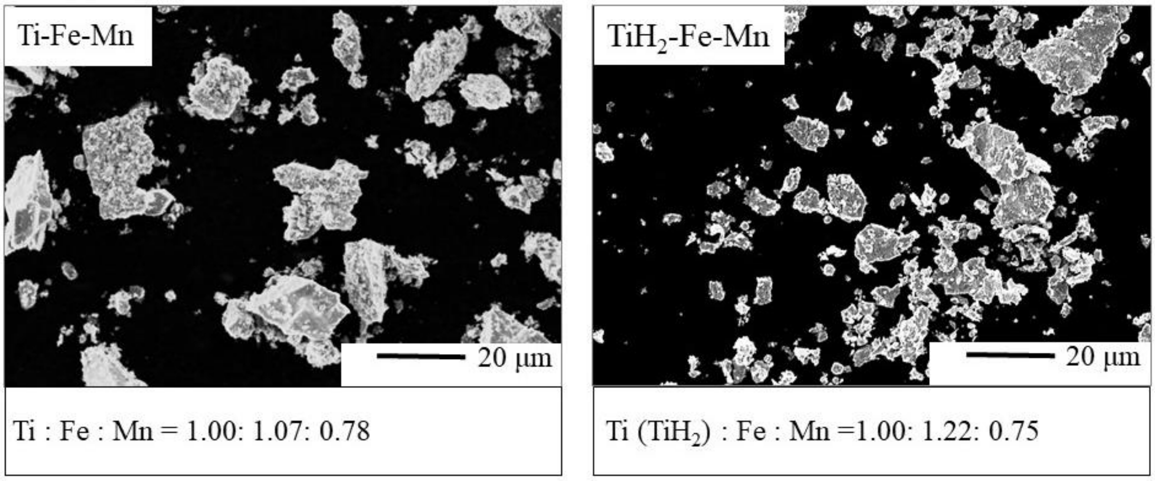

Fig. 31 SEM images of samples with Ti-Fe-Mn and TiH_2-Fe-Mn powders after 100h of MA under atmosphere of hexane super dehydrated, with compositions determined by EDS.

Fig. 32 shows the XRD results. It can be seen that when TiH_2 is used, multiple phases are seen and the composition is not single, while when Ti is used, a single alloy phase is formed under the same conditions. In the case of TiH_2 is used, the single-phase peak of TiH_2 remains.

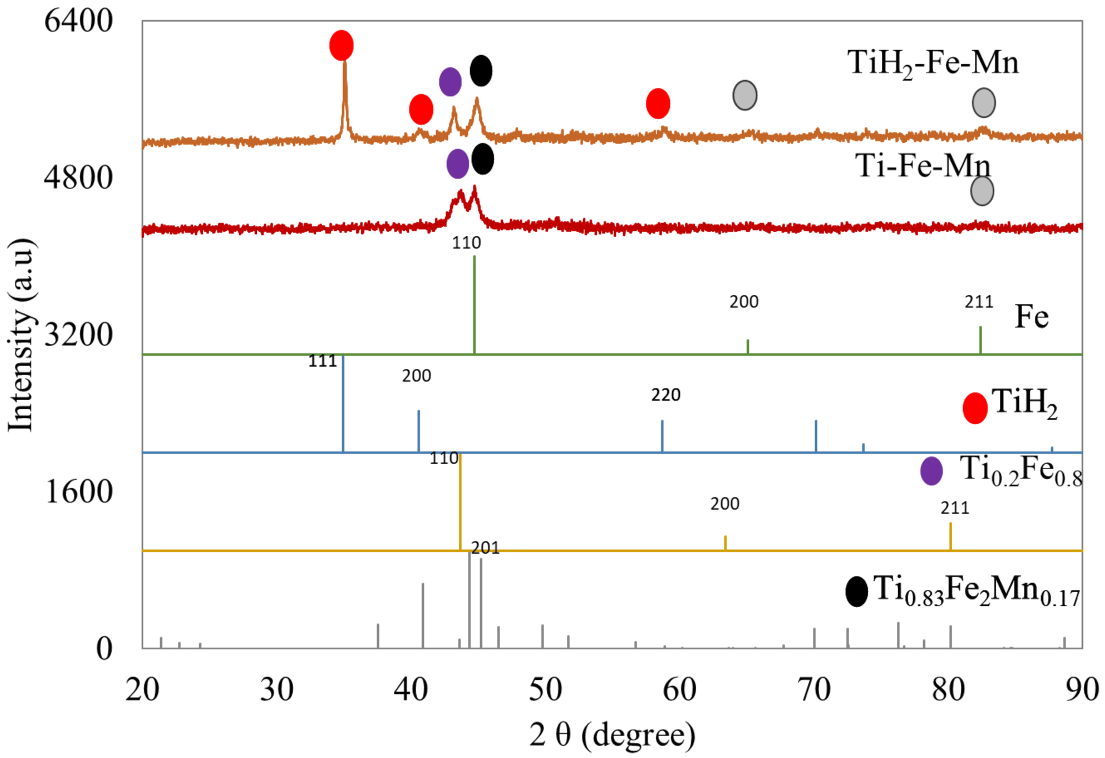

Fig. 32 XRD of samples made with Ti-Fe-Mn and TiH_2-Fe-Mn powders after 100 h of milling under an atmosphere of hexane super dehydrated

Thin films such as rare earth lose their metallic luster when hydrogenated and become permeable [26]. The covalent bond or the ionic bond becomes more vital in the metal hydride phase; the metal bond is lost accordingly. It is also the reason why TiH_2 mechanically loses ductility and becomes more brittle. When TiH_2 is used as the starting material, although an oxide layer exists on the outermost surface of the TiH_2 particles, the covalent bond is stronger than the metal bond because the hydride phase is directly under the oxide layer. Therefore, the bond between TiH_2 is stronger. It is presumed that the free electron density decreases as the number of electrons contributing to MA increases, including near the surface. It is difficult for crystals to fuse even when particles collide violently due to mechanical impact in MA. Higher energies are expected to be required for crystal fusion [27].

The result of the total experiment is summarized in Table 13. Alloy phase partially compounds in the case of Ti-Cr-Mn and TiH_2-Cr-Mn at 50h, TiH_2-Cr-Mn and TiH_2-Fe-Mn at 100h. Alloy phase compounds in Ti-Cr-Mn and Ti-Fe-Mn at 100h.

Table 13 Result of XRD analysis of samples milled by wet type

Milling time	Ti-Cr-Mn	TiH_2-Cr-Mn	Ti-Fe-Mn	TiH_2-Fe-Mn
10 h	×	×	×	×
20 h	×	×	×	×
50 h	△	△	×	×
100 h	○	△	○	△

○ Alloy phase compound △ Alloy phase partially compound × Alloy phase not compound

5.3.4. Effect of Mn on the preparation of Ti-based alloys

In the TiCrMn system, Cr and Ti or TiH_2 are observed as a simple substance with a MA time of 10 h, and Mn cannot be confirmed, and it is presumed that they exist in a state close to amorphous. Similarly, in the case of the TiFeMn system, the Mn of the carrier was not observed, and the composition after 100 h showed smaller values than Ti and Fe (Fig. 32).

Previously, when performing MA in dry condition by Ar atmosphere using a stainless steel mill pot, most of the Mn reacted with the pot wall, causing a reaction that caused the pot's inner diameter to shrink unevenly, resulting in a large Mn composition. In this work, it was found that the reaction between the pot wall and Mn was significantly reduced by using dehydrated hexane instead of Ar as the MA environment. In the case of TiFeMn-based alloy prepared by MA, it is considered that Mn reacts with the pot wall even when dehydrated hexane is used. In the TiCrMn system, the $TiCr_2$ phase is generated at an early stage, and it is presumed that Mn is taken in more easily than the stainless steel surface, which does not affect the composition after 100 h. We suggest that the reason is the fact that TiFe is hard than $TiCr_2$. Further studies are needed on the reaction with the pot wall.

5.4. Summary of chapter

In this research, Ti-based alloys were prepared alloy by MA using a ball-milling process. We have obtained TiCrMn alloys from a mixture of Ti, Cr, and Mn using different ball milling times with hexane (super dehydrated). It was shown that a dispersion medium like hexane is necessary to avoid fixation of the powders in the milling pot. By using this wet type ball milling process, the composition of the alloys could be controlled. We have successfully achieved a target with a composition after 100 h of milling with an atomic ratio of 1 : 1 : 1. This method has the potential for mass production of TiCrMn and offers a chance to utilize hydrogen storage alloys as a model of a hydrogen carrier. Moreover, chemical composition, crystal structure, and grain size might be controlled by changing the milling time to improve the hydrogen storage property.

In this research, the effects of using metallic titanium and TiH_2 as a starting material when synthesizing Ti- based hydrogen storage material by mechanical alloying by the ball milling method were examined using the XRD analysis method. It was clarified that when Ti is used, an alloy having a target composition can be more easily synthesized under the same MA conditions for both Ti-Fe-Mn and Ti-Cr-Mn as compared with the case where TiH_2 is used. In the hydride phase of Ti, the metal property is lost due to the low density of free electrons including the vicinity of the surface due to the formation of the bond between Ti and H, and the metal homology occurs in the mechanical collision in the MA process. In the future, in the synthesis of Ti-based alloys by mechanical alloying, it is considered that it will be possible to synthesize hydrogen storage materials faster by using metal Ti instead of TiH_2, that is, with less input energy.

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Chapter VI: LIFE CYCLE ASSESSMENT (LCA) of HYDROGEN ENERGY SYSTEM (in case of KAZAKHSTAN)

6.1. LCA of Hydrogen Energy System for energy supply

Life Cycle Assessment is a systematic tool to analyze the environmental impact of a product through all stages of its life cycle, from the extraction of resources to the production of materials, parts and the products itself, and its management after it is discarded, either by reuse, recycling or final disposal. LCA compiles and evaluates the inputs and outputs and the potential environmental impacts of a product system throughout its life cycle.

IDEA (Inventory Database for Environmental Analysis), is a Japanese database that mainly uses national and some international statistics as its data source and aims to model the environmental impacts [1]. Unfortunately, the data for Kazakhstan is not available. To compare and see the general environmental impact, IDEA v2 was chosen.

We took into account the available CO_2 emissions from each process in Hydrogen Energy System in case of Kazakhstan by based on IDEA soft dates and other references.

We consider processes such as, construction of solar power 1kWh; production of 1kg metals (Ti, Cr, Mn, Fe) [1]; preparation of alloy by MA (1000h /10^5kg) [2], transportation by freight train (10^3m/10^3 kg per km) [3].

According to IDEA soft dates construction of solar power 1kWh considers construction materials (Polyphenylene ether resin, aluminum paste, pure water, ion exchange membrane method, polished plate glass, concrete, carbonized silicon, ordinary steel, steel pipe, wire silica steel sheet, power cable, etc.) and from construction to completion of civil engineering structures in Japan.

Production of 1 kg Ti was performed by using the mining of titanium ore (mineral sand) in Tamil Nadu, India, as a model case. The importing partner country's material flow and energy input was estimated from data such as existing literature, set equipment specifications, operating conditions, etc. The result shows the process of dredging and mining mineral sand.

Production of 1 kg Cr was considered chromium ore/concentrate, carbon reduction, dissolution, iron removal, electrowinning processes. Raw material input, energy input, and emissions are calculated from the process contents described in the environmental load calculation survey at the refining stage of metal elements.

Production of 1 kg Mn was analyzed from reduction soaking, leaching, electrowinning in Mn smelting in the USA, South Africa, Russia, China.

Production of 1 kg Fe has assumed the average casting method in Japan in 2010.

Ball milling and transportation by freight cars are calculated by energy consumption if the energy source is coal.

We calculated considering the values listed in Table 14 the CO_2 emissions for the Hydrogen Energy System in Kazakhstan, which was more than 20 times less than present CO_2 emissions for electricity coal.

Table 14 CO_2 emissions of corresponding process delivered form calculation using IDEA data (energy supply)

Process	CO_2 (kg)	Consumption/year (for 10^6 capita)	CO_2 (kg) for HES
Construction of solar power 1kWh	5×10^{-2}	1.04×10^{11} kWh /year	5.2×10^{8}
Production of Ti 1kg	9.2×10^{-5}	10^{7} kg	9.2×10^{2}
Production of Cr 1kg	5.9×10^{-3}	10^{7} kg	5.9×10^{4}
Production of Mn 1kg	5.9×10^{-3}	10^{7} kg	5.9×10^{4}
Production of Fe 1kg	1.1×10^{-1}	10^{7} kg	1.1×10^{6}
Ball milling 1000h /10^{5}kg	7.2×10^{2}	3×10^{7} kg	2.2×10^{4}
Freight train 10^{3}m/10^{3} kg per km	2.5×10^{-2}	6×10^{5} m/ 3×10^{7} kg	1.5×10^{8}
Fuel-cell	0	2.0×10^{9} kWh	0
Total for HES in KZ			**6.7×10^{8}**
Present electricity	3.5×10^{-1}/kWh	5×10^{9} kWh	1.4×10^{10}

6.2. LCA of Hydrogen Energy System for water transportation

As mentioned in Chapter1, tap water is not safe to drink in Kazakhstan, and around 30% of consumers completely abandon it, preferring to buy bottled water. Hence, 9×10^5 m^3 per year of bottled water is transported in large cities [4]. PET (Polyethylene terephthalate) bottles are commonly used for the packaging of bottled water. Plastic problems are occurring in many countries. LCA of PET is one of the main themes from the end of the 20th century even now [5-6]. Depending on the country, the characteristics of PET bottles are different. For instance, the weight of the bottle of 1.5 L water in Saudi Arabia is 32.6 g [7], 41g in Russia [8]. Japan has set a reduction target for the PET bottles. As a result, the overall weight was reduced by 23.6% in 2018 [9]. In Kazakhstan, the weight of the bottle is 42-44 g [10].

We took into account the available CO_2 emissions from water transportation with the PET bottle by train. IDEA soft dates and other references are considered and the amount of CO_2 emissions is calculated and compared. CO_2 emissions during water transportation by PET bottle via railway were 3 times less than Hydrogen Energy System (Table 15). However, by considering the difference of characteristics of PET bottle in Japan and Kazakhstan, we suppose the almost same amount of CO_2 will be emitted. Moreover, the utilization of a large number of plastic bottles has another negative effect on the environment.

Table 15 CO_2 emissions of corresponding process delivered form calculation using IDEA data (water transportation)

Process	CO_2 (kg)	Consumption/year (for 10^6 capita)	CO_2 (kg) for water transportation
Bottled water 0.001 m^3	1.0	1.3×10^6 m^3	1.4×10^6
PET bottle 1 kg	5.5	3.7×10^7 kg	2.1×10^8
Freight train 10^3m/10^3 kg per km	2.5×10^{-2}	1.3×10^9 kg	3.3×10^4
Total for water transportation			2.1×10^8
Total for HES in KZ			**6.7×10^8**

6.3. Summary of chapter

The LCA result confirms that hydrogen is considered to be an ideal energy carrier in the future and can play a considerable role in the energy system of Kazakhstan. Particularly, CO_2 emissions for the Hydrogen Energy System in Kazakhstan, which was more than 20 times less than present CO_2 emissions for electricity coal and almost the same with water transportation by PET bottle via railway.

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Chapter VII: CONCLUSIONS

7. Conclusions

With the spread of activities related to the SDGs, the realization of a sustainable society is expanding worldwide. The SDGs are concrete action goals for realizing a better and more sustainable future for the planet.

In particular, in order to break away from the social system caused by the mass consumption of fossil fuel energy resources, it is urgently necessary to improve the QOL of people around the world. Since the Industrial Revolution, we have lived a life dependent on fossil fuel energy resources worldwide. The mass consumption of fossil fuel energy resources has led to various environmental and pollution problems, including global warming. Especially after the COVID-19 pandemic, our planet has to move toward rebuilding their lifestyle, economies, and recovery plans that can shape the 21st-century economy in clean, green, healthy, safe, and more resilient ways.

In this research, SDGs Goal 6 (safe water worldwide) and Goal 7 (energy for everyone) are taken as examples. In the introduction of renewable energy, a system using hydrogen as an energy medium is taken up as energy. We proposed a quantitative model that links the supply of energy and the supply of drinking water.

Kazakhstan, which is frequently in short supply of drinking water, was used as an example, and we examined the feasibility of environmental conservation efforts, improvement of the energy situation, and the solution of water problems. As an approach to that, we took up hydrogen energy and examined the use of hydrogen as an energy medium and a water source.

Kazakhstan is a country located in the central part of the Eurasia, which is rich in natural resources, has an energy self-sufficiency rate of 209%, most of which, 99%, is fossil fuel energy resources. With the expansion of life dependent on fossil fuel energy resources, it has become a cause of air pollution, water pollution, and global warming. Furthermore, the water supply system's infrastructure was constructed under the Soviet Union in the 20th century. Despite its aging, it is still in use, and in large cities, water is currently obtained from the nearest river. About half of the inflowing river water comes from neighboring countries. The amount of inflowing river water decreases and is more polluted every year due to agricultural use in those countries. Under these circumstances, supplying drinking water from limited water resources to metropolitan areas and drinking water supply has become a significant issue.

A Hydrogen Energy System is modeled for the city, far away from a place with much solar radiation and suitable water sources. The hydrogen system consisted of renewable energy, a water tank, an electrolyzer, a hydrogen storage alloy tank, transporting hydrogen storage alloy tank by railway, and utilization of hydrogen by fuel cells without a negative impact on the environment.

Electricity generated from renewable energy is inputted to the electrolyzer for electrolyzing water and producing hydrogen directly. Renewable energy-driven hydrogen generation is a favorable way. The electricity consumption per capita is 5000 kWh/year in Kazakhstan. If hydrogen energy becomes a conductor of energy, 1.34m^3/year of water will be necessary as a hydrogen source.

The energy consumption per capita in Kazakhstan is 5000 kWh/year, which can get by 7.44×10^4 mol /year of hydrogen. To produce this amount of hydrogen, we need 1.34 m^3/year of water, 5.82×10^3 kWh of energy, which comes from 8.31×10^3 kWh /year of power consumption by electrolyzer, and 5.19 ×10^4 kWh/year of solar energy from solar cells with 34.6 m^2 of surface area.

To create a hydrogen energy system, we need a practical consideration of hydrogen production, storage, and utilization that does not significantly impact the environment. Nowadays, the technologies for the production and use of hydrogen have been found, and efficiency and cost problems have been identified. Also, to use hydrogen in practice, it is necessary to consider a reliable and stable method of storing and transporting it.

The development of an appropriate hydrogen storage technique is one of the most critical problems of hydrogen energy. Hydrogen can be stored and transported by different methods from the point of production to the point of use.

We considered hydrogen storage alloys as hydrogen carriers with high structural stability and hydrogen storage capacity in this contribution. Hydrogen storage alloys have attracted considerable attention because they are safe and efficient media for transporting hydrogen energy. Since hydrogen storage alloys are heavy, they can be transported by rail safely, consequently increasing the amount of hydrogen transported in the existing infrastructure.

Produced hydrogen will provide storage to Ti-based hydrogen storage alloy because Kazakhstan has substantial resources of Ti, Cr, Fe, Mn, and their prices are lower than rare earth metals, which are commonly used for hydrogen storage material. A Ti-based alloy will be prepared by MA, then transported by railway.

We assume the weight of transported hydrogen storage alloy per wagon is 5.4×10^4 kg with 1.5 wt% of hydrogen. The hydrogen capacity per wagon is 4.1×10^5 mol. If a regular train is composed of 50 wagons, 2.04×10^7 mol H_2 will be transported. If a train transports it 10 times per day, they transport 2.04×10^8 mol of H_2/day and 7.4×10^{10} mol /year. Approximately 3×10^7 kg/year of the alloy will be used.

The hydrogen energy system for water transportation is available by utilizing fuel cells for hydrogen utilization. Finally, more than 1 million people are provided with water and 0.4 million people with electricity by utilizing fuel cells. The system is also capable of satisfying drinking water requirements, and society can become practically self-sufficient.

The TiFeMn alloy can be considered one of the attractive hydride forming materials from the technological view. It is promising to use industrial application due to several advantages such as moderate hydrogen absorption conditions, relatively high hydrogen storage capacity, and their abundance. This study considered characteristics of TiFeMn prepared by MA method for mass production, improved activation process by heat treatment methods such as 673 K under hydrogen pressures over 2.7 MPa in 15 min. As a result, pressure, temperature, and time are decreased compared with TiFe prepared by arc melting and mechanical alloying. However, alloy prepared by MA after hydrogenation is not resistant to oxidation, like casted alloy. It needs to be recovered. Experiment results confirmed that a catalyzer such as Pd/Al_2O_3 affects oxidation.

In this research, Ti-based alloys were prepared alloy by MA using a ball-milling process. We have obtained TiCrMn alloys from a mixture of Ti, Cr, and Mn using different ball milling times with hexane (super dehydrated). It was shown that a dispersion medium like hexane is necessary to avoid fixation of the powders in the milling pot. By using this wet type ball milling process, the composition of the alloys could be controlled.

In this research, the effects of using metallic titanium and TiH_2 as a starting material when synthesizing Ti- based hydrogen storage material by MA were examined. It was clarified that when Ti is used, an alloy having a target composition can be more easily synthesized under the same MA conditions for Ti-based alloys as compared with the case where TiH_2 is used. In the hydride phase of Ti, the metal property is lost due to the low density of free electrons, including the vicinity of the surface due to the formation of the bond between Ti and H, and the metal homology occurs in the mechanical collision in the MA process.

Generally, this research supposes the role of the hydrogen energy system in Kazakhstan for renewable energy dissemination and greenhouse gas emission reduction and effective water resource utilization. A possible hydrogen system in Kazakhstan was modeled in hopes of decreasing the amount of greenhouse gas production. The LCA result confirms that hydrogen is considered an ideal energy carrier in the future and can play a significant role in Kazakhstan's energy system. CO_2 emissions for the Hydrogen Energy System in Kazakhstan, which was more than 20 times less than present CO_2 emissions for electricity coal and almost the same with water transportation by PET bottle via railway.

The system is also capable of satisfying potable water requirements, and society can become practically self-sufficient. In the future possibilities of fuel cell train, utilization of fuel cells works not only in large cities, but rural areas are also given a significant opportunity to supply water. The water supply system considered here can be generalized to other countries with water shortage problems, even in other planets in the future.

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