The Research Progress on Preparation of Al-Ti Alloy

X D Wei, H M Kan*, X Sun, N Zhang, X Y Wang and H B Long
The Liaoning Provincial Key Laboratory of Advanced Materials & Preparation Technology, Shenyang University, Shenyang, China

Abstract. Al-Ti alloys are widely used in various fields due to their excellent properties. There are mainly four production methods for Al-Ti alloys, namely direct dissolving method, sintering method, reduction method and electrolytic method. The first three preparation methods all have high-temperature melting steps, which increase energy consumption and production costs, generate hydrogen evolution or segregation, and reduce the quality of the Al-Ti alloy coating. There are three types of electrolysis systems, namely organic solvent systems, ionic liquid systems, and inorganic molten salt systems. Apart from the inorganic molten salt system, the organic solvent system and the ionic liquid system have the advantages of lower energy consumption, lower production cost, and uniform Al-Ti alloy coating prepared by electrolysis. Among them, the ionic liquid system has good chemical stability, good thermal stability, low energy consumption, and can be recycled.

1. Introduction
Due to its rich content in the earth's crust and its low density, Al is widely used. However, if Al and Al alloys grains are too large, their mechanical properties will be affected[1]. Grain refinement is an effective method to improve the quality of Al and Al alloy[2-4]. The most effective method is to add a grain refiner to Al[5]. The following elements can be added, such as Ti, Zr, V, B and Cr. Ti is one of the most significant elements. Rosenhain et al.[6] discovered that Ti was added to Al in the 1930s, and the effect of grain refinement was obvious. It can be used as a grain refiner to study. Most developed countries use Ti to refine grain, especially in the field of casting of Al alloy. Nearly 100% of the alloy is refined through the alloying of Ti and Al. Addition of transition metals and rare metals such as Ti, Mn or Cr in Al reduces the probability of pitting corrosion in the chloride ion medium. Adding a small amount of Ti element to Al alloy can effectively improve the strength, wear resistance, machinability, castability and thermal conductivity of the Al alloy, and reduce its expansion coefficient[7-8].

Al-Ti alloy has many excellent properties, such as higher specific strength, better oxidation resistance, corrosion resistance and biocompatibility[9-10]. It is widely used in aerospace, automotive and electronics products and other fields[11-14]. However, due to the low electronegativity of Al and Ti, it is difficult to be electrolyzed in aqueous solution, which is also an important factor limiting the development of Al-Ti alloy.

2. Al-Ti alloy preparation method

2.1. Direct solvation method
The direct solvation method is one of the most used methods in actual production of Al-Ti alloys. This production method is to melt Al and Ti pure metals in a high temperature melting furnace according to a certain ratio. Then a certain production process is used for the production of Al-Ti alloy.
The advantage of this method is that it is simple to operate. However, this production method needs to be heated in a high-temperature melting furnace. Al-Ti alloy will cause chemical reactions with water, oxygen, and other substances in the air during the production process. Thereby hydrides are generated; the energy consumed in the production process is large and the grains on the surface of the coating are not uniform, the production cost is increased. This preparation method also has the disadvantages of poor corrosion resistance, environmental pollution and poor recovery of Ti.  

2.2. Sintering method

Sintering is a method of powder metallurgy. Among them, the SHS method, XD method, and mechanical milling-reaction sintering method are the main process methods. The mixture of Al powder and TiO2 is added in a metallurgical furnace, then a reducing agent is added. Finally the material in the metallurgical furnace is sintered to produce Al-Ti alloy.  

The sintering temperature, sintering time and grain size are reduced effectively by this method. It has been widely concerned. However, the requirements for processing equipment are high and the production cost is high[19]. The Japan Institute of Defense[20] has successfully prepared high-hardness TiAl intermetallic compounds by using a spark-sintering method. The hardness of it is as high as 10kN/mm² to 12kN/mm², which is about 6 times that of conventional compounds.

2.3. Reduction method

The reduction method is a production method of producing Al-Ti alloy according to the aluminothermy method. In this method, TiO2 is added to pure metal Al to produce pure metal Ti, then processed to be Al-Ti alloy. The process includes three steps. Firstly heating and melting in a crucible resistance furnace, and then mixing. Secondly, the mixed material is added to the Al melt, stirred, heated and kept warm. Finally the alloy is fully reacted, and then stirred[21].  

This method is not subject to temperature restrictions and the Al-Ti alloy obtained has a high Ti content. However, when melting at high temperatures, Al-Ti alloy is prone to high temperature oxidation and inclusions. This preparation method is inappropriate to be mass-produced and the production cost is high. Cao Dali et al.[22] used TiO2 as a raw material and Al as a reducing agent in the cryolite melt. Temperature was controlled between 1150°C and 1300°C. Al-Ti alloy master alloy containing 7.13% to 11.08% by mass of Ti.

2.4. Electrolytic method

Electrolysis method is usually used to prepare metal coatings with special functions. The electrolytic method can effectively improve the surface properties of metals such as oxidation resistance, corrosion resistance, electrical conductivity, and non-magnetic properties. Since the chemical activity of H is more narrow than that of Al and Ti and the chemical window of water is relatively narrow. If the Al-Ti alloy is prepared in an aqueous solution, hydrogen evolution occurs and the quality of the Al-Ti alloy coating will be affected[23-24]. In 1983, Japan's NEC Corporation[25] produced an Al-Ti alloy solid electrolytic capacitor. Yu Xuguang et al.[26] added TiO2 to prepare Al-Ti alloy on the basis of industrial Al production at 960°C. It uses graphite as an electrolytic cell, cathode and anode, Na3AlF6-Al2O3 as electrolyte to successfully electrolyze Al-Ti alloy. This method is compared with the traditional method by first preparing Ti by reduction method and then making Ti and Al melt Al-Ti alloy. This method has the advantages of less production links and effective reduction of energy consumption and production cost required for production[27]. Gao Xizhu et al.[28] added the mixed Al2O3 and TiO2 to an Al electrolytic cell under the conditions of industrial Al electrolysis (between 950°C and 970°C), successfully produced Al-Ti alloy.

The electrolytic method makes it possible to produce large quantities of Al-Ti alloy in China, effectively saves energy. It is not only possible to use overproduction of titanium dioxide, but also not to upgrade the technical requirements and procedures for the original equipment, and effectively saves the cost of Al-Ti alloy. As a more advanced production method for preparing Al-Ti alloy, the electrolytic method also effectively reduces the probability of hydrogen evolution and inclusion.
However, the Ti content of Al-Ti alloy prepared by electrolysis is generally between 0.5% and 2.0% and the Ti content is low\[^{[29]}\].

2.4.1 Organic solvent system.

The AlCl\(_3\)-LiAlH\(_4\) system is commonly used in organic solvent systems, which is known for its simplicity of operation and high purity of the coating. However, this system is volatile and flammable\[^{[15]}\]. In addition to the AlCl\(_3\)-LiAlH\(_4\) system, the organic solvent system also includes the AlBr\(_3\)+HBr/KBr system and the Al(C\(_2\)H\(_5\))\(_3\)+NaF system. The former has a lower purity but less volatility and the latter has a high purity but cost is also high. In the early 1990s, Biallozer\[^{[30]}\] studied that the deposition rate is the highest and the quality of the coating is good when the mole ratio of AlCl\(_3\) to LiAlH\(_4\) in the AlCl\(_3\)-LiAlH\(_4\) system is equal to 1. Therefore, catalysts can be used in the AlCl\(_3\)-LiAlH\(_4\) system to increase the reaction rate and coating quality when electrodepositing Ti-Al alloy.

2.4.2 Molten salt system.

The molten salt system includes room temperature molten salt and high temperature molten salt. It is also known as ionic liquid system and inorganic molten salt system.

- Ionic liquid system.

  Ionic liquid systems are used to prepare metals that are electrolyzed difficultly in aqueous electrolytes, such as Al, Mg, and Ti\[^{[31-32]}\]. This system has the advantages is the operation is simple and Al-Ti alloy composition is uniform. The ionic liquid is mainly composed of anions and cations. The density, melting point, viscosity, acidity and alkalinity, and thermal stability are all related to the radius or modulus of the anions and cations. This system has good chemical stability and thermal stability, low energy consumption, and can be recycled repeatedly. So the ionic liquid is also called green solvent.

  AlCl\(_3\)-EMIC ionic liquid system is the most commonly used at present. And it is also the best ionic liquid system for electrical conductivity. Lu Yunshu et al.\[^{[27]}\] prepared Al-Ti alloy successfully in the [Bmim]Cl:2AlCl\(_3\) ionic liquid system at room temperature. Ti ions was introduced by adding TiF\(_4\), and three electrodes (working electrode: Ag, diameter 2mm, purity 99%; Reference electrode: Al wire, diameter 6mm, purity 99.999%; counter electrode: Al-Ti alloy) were used.

- Inorganic molten salt system

  The difference between the inorganic molten salt system and the ionic liquid system is that the ionic liquid is conducted at room temperature, and the inorganic molten salt system is performed at a high temperature. So its energy consumption is higher. The inorganic molten salt system has the advantages of simple operation and uniform plating. But it also has the disadvantages of high energy consumption and low deposition efficiency\[^{[33-35]}\]. Guo Jiaju et al.\[^{[36]}\] successfully prepared Al-Ti alloy in the low-melting-point molten salt system of titanium chloride and aluminum chloride at 180°C. Al and Ti plates with a purity of 99.9% were used as anodes, and Ti bars were used as cathodes. Density was controlled in the range of 0.03A/cm\(^2\) to 0.3A/cm\(^2\). It was observed that the cathode current density was different and the morphology of Al-Ti alloy was different. According to the difference of Ti content, Al-Ti alloy can be divided into three structures. When the Ti content is lower than 23%, Ti
is a solid solution structure in Al. When Ti content is 31%, it is Al-Ti intermetallic compound. At 44%, it is similar to Al-Ti intermetallic compounds. Xiao Yihua et al.[34] used TiO₂ to prepare Al-Ti alloy at high current density in aluminum electrolytic cell.

Figure 3. SEM image of electrodeposited Al-Ti Alloy in [Bmim]Cl:2AlCl₃+0.2MTiCl₄ system.

3. Application prospect of Al-Ti alloy

- Application in aerospace.
  Due to its low density, high specific strength, good wear resistance and good corrosion resistance, Al-Ti alloy has been widely used in recent years to reduce the weight of aerospace equipment (aircraft, aircraft carriers, spacecraft, etc.) and the degree of external corrosion. The use of Al-Ti alloy in the aircraft’s impeller reduces its weight by 20% and improves the wear resistance and corrosion resistance of the impeller[37-38].

- Application in automobile.
  With the improvement of the economic level, people's demand and requirements for automobiles are also getting higher and higher. Al-Ti alloy can be used to reduce the weight of automotive substrates to achieve energy-saving and emission-reduction effects. The United States and Japan have invested to study the application of lightweight materials in the automotive field. One of the automotive hub materials is Al-8Ti alloy. With the continuous development of human economic level, the requirements for the creep resistance of automotive hub materials have also been continuously increased. It is possible to add different contents of Sr and Sb alloy elements to Al-8Ti alloy[39] to improve the creep resistance of automobile wheels. High-reflection Al-Ti alloy is also used in rear view mirrors.

- Application in electronic products.
  In recent years, Al-Ti alloy has been gradually applied in the field of electronic products. Al-Ti alloy can be used as mobile phone casing materials and also used by IBM for the casing of notebook computers. With the continuous development of the economy, people's demand for mobile phones and computers is also growing. Today, one person has one mobile phone, one computer, or multiple mobile phones, multiple computers. Therefore, Al-Ti alloy is also used in electronic products. that will become a development direction that it cannot be ignored.

- Application in medical field.
  Al-Ti alloy has advantages such as low density, non-toxicity and good biocompatibility and are widely used in the medical field. It is used to make human bones or artificial limbs, providing more possibilities for those who need it. Nowadays, there have been many studies on the corrosion resistance of Al-Ti alloy as human bones[40-41].

4. Conclusion

- The preparation methods of Al-Ti alloy mainly include direct melting, sintering, reduction and electrolysis. The above three methods for preparing Al-Ti alloy has more energy consumption and higher production costs, and are prone to hydrogen evolution and cause segregation of Al-Ti alloy.

- There are three major electro deposition systems, ionic liquid systems, inorganic molten salt systems, and organic solvent systems. Among them, the inorganic molten salt system needs to be carried out at a high temperature and has high energy consumption. The organic solvent system has the disadvantages of being volatile, flammable and explosive. The low energy consumption and thermal stability of ionic liquid systems are particularly prominent.
Al-Ti alloy has excellent physical and chemical properties such as specific strength, oxidation resistance, corrosion resistance and biocompatibility. It has broad application prospects in aerospace, automotive, medical, and e-commerce.

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