CURRENT STATUS OF CARBIDIC AUSTEMPERED DUCTILE IRON

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Abstract. Grinding balls in wet ball mill are important consumables in mine grinding equipment, which have poor wear resistance and large consumption. It is imperative to find excellent wear-resistant materials for the grinding balls. Carbidic Austempered Ductile Iron (referred to as CADI) was used as small and medium-sized wet ball mills. This grinding ball has the advantages of less wear, low crushing rate, power saving and low noise. However, the CADI grain boundaries are distributed with net-like eutectic carbides, which seriously damage the continuity of the matrix. In addition, the mechanism of corrosion wear and impact fatigue is lack of research due to complex phase composition and unclear mechanism of phase properties on improving performance. So CADI can't be applied to the grinding balls in large wet ball mill. Based on the above problems, this paper first analyzed the heteronucleation mechanism and adsorption mechanism of M_3C type carbides by using the first principle of microalloying elements, and then verified it by combining with experimental results. Then the thermodynamics and kinetics of austenite homogenization and isothermal transformation of ductile iron containing carbides were analyzed by means of modeling calculation and experiment. On this basis, a new type heat treatment process comprising super-high temperature pretreatment and austempering treatment (S&A treatment) was used to process CADI, which provides a new idea for further improving toughness of CADI. Finally, the CADI corrosion wear and impact fatigue failure mechanism were revealed by analyzing the change rule of the sample surface and cross section after corrosion wear and impact fatigue.

1 Introduction

Wear-resistant materials are indispensable consumable materials in the industrial field. The production of wear-resistant parts is mainly realized by casting method, with large consumption and wide application. For example, the ball mill of metallurgical mine is one of the important parts in the grinding equipment. However, due to the violent collision and relative movement between the ball and the ball, and between the ball and the lining plate in the ball mill, the ball is subjected to repeated impact, extrusion and grinding, leading to the main failure forms of large diameter ball wear, crushing and loss of roundness. The internal cause of grinding ball failure is the hard contradiction between hardness and toughness of grinding ball. At present, the wet grinding balls commonly used in China's mines are mainly alloy cast iron balls and forged (rolled) steel balls. Most of the grinding balls used in foreign mines are forged (rolled) steel balls, which occupy more than 70% of the grinding ball quantity. Most of the grinding balls used in domestic mines are low chromium white cast iron balls containing less than 5%Cr. Due to the large potential difference between the substrate and carbide in low chromium white cast iron, electrochemical corrosion is prone to occur in the corrosive medium[1], which intensifies the spalling of carbide. Low chromium cast iron grinding balls are easy to crack and flake.

In recent years, on the basis of austempering ductile iron (ADI), by adding a small amount of strong carbide forming elements (such as Cr, Ti, V, Nb, etc.) and developed with carbide (CADI), isothermal quenching nodular cast iron has good casting performance, small density, wear-resisting corrosion resistance and the lower cost of production advantages, used as mine wet grinding medium and small ball mill grinding balls, It shows advantages of less abrasion, low crushing rate, power saving and low noise [2-4].However, compared with forged (rolled) steel balls, CADI grinding balls still have low strength and toughness. When used in large wet grinding ball mills in mines, CADI grinding balls have high crushing rate, resulting in reduced grinding efficiency.

This paper will contain carbide isothermal quenching nodular cast iron as a wet mill grinding ball material, through regulating the strengthening phase carbide quantity, shape, scale and distribution, control matrix organization austenitic austenitic carbon content and the number and acicular ferrite scale, so as to improve the hardness of CADI, impact toughness, wear resistance, fatigue resistance, corrosion and wear resistance, etc. It provides theoretical and technical support for CADI to manufacture mill ball of large scale wet mill in mine. In addition, the ball of large wet mill is subjected to the interaction of impact, wear and corrosion at the same time. It has important practical significance to study the failure mechanism of the ball under the interaction of different impact loads, different corrosive media and different wear modes.

2 ADI research progress

Isothermal quenched ductile iron (ADI) has excellent comprehensive mechanical properties [5-8].Because the fluidity of ductile iron is obviously better than cast steel, in many cases, it can be used to replace cast steel and forged steel made of various complicated shapes, large force, easy to wear parts, has developed into an indispensable engineering material. The research on ADI began in the early 1970s and has been widely used in automobile, construction, mining, agricultural machinery and railway. After more than 40 years of development, in North America, Europe and China have a more mature process. ADI has the advantages of high strength, high hardness, good plasticity, superior fatigue resistance and wear resistance and good vibration damping. In recent years, ADI has developed rapidly and its application scope has been gradually expanded. In western industrial developed countries, ADI production has increased at a high rate of 15% per year in the past decade. American Society for Materials and Testing (ASTM) revised the ADI standard and established six grades. As one of the earliest countries in the world to develop ADI, China has witnessed rapid development and promotion of ADI. Currently, the annual output of ADI is more than 100,000 tons, which is not only used in grinding balls and lining boards, but also used in cars and other heavy truck chassis parts.

Chemical composition and heat treatment process are important factors affecting ADI mechanical properties. Chemical composition, including the basic elements (C, Si, Mn, P and S) and common alloying elements (Cu, Ni and Mo, etc.) in ductile iron. In terms of heat treatment process, the formation process of ADI can be analyzed from the perspective of heat treatment process belt. At the beginning of isothermal transition, acicular ferrite increases gradually with the passage of holding time. Due to the large amount of Si in nodular cast iron, carbide precipitation is inhibited. With the formation of acicular ferrite, excess carbon elements are enriched into residual austenite. The first stage of austenite transformation occurs when the carbon content of the retained austenite is enriched to a degree that it is stable enough at room temperature. When the holding time is long enough, the residual austenite is stable enough to decompose into ferrite and carbides, resulting in reduced toughness, which is the second stage of austenite transformation. Therefore, the area between the two stages is called the "heat treatment process zone".

In the past decades, researchers have fully discussed the influence of heat treatment process parameters on the microstructure and properties of ADI, and studied the thermodynamic characteristics and dynamics of heat treatment process. Putatunda et al. [9] analyzed the influence of different austenitizing temperatures on ADI fracture toughness, and found that austenitizing temperatures over 982°C would seriously reduce the fracture toughness of materials. Delia et al. [10] studied the influence of austenitizing temperature and holding time on ADI, and found that a shorter austenitizing time would lead to a higher impact toughness, while the impact toughness would decrease with longer holding time. Wang et al. [11] studied the influence of isothermal temperature on the austenite matrix and found that grain size increases with the increase of isothermal temperature. When the isothermal temperature is 240°C, the relationship between austenite and ferrite follows the Greninger-Troianorelation.The NishiyamaWassermann relation and greninger-Troiano relation are followed between austenite and ferrite. Sellamuthu et al. [12] explored the influence of isothermal temperature on ADI performance. The results show that the hardness, strength and wear resistance of ADI decrease with the increase of isothermal temperature, but the plasticity and impact toughness increase. When the isothermal temperature is between 340 °C and 360°C, ADI can obtain the best comprehensive mechanical properties. Wang et al. [13] conducted rolling contact fatigue experiments on ADI prepared at different isothermal times by using a double-plate rolling forming machine. They found that with the increase of holding time, the hardness of isothermal quenched nodular cast iron gradually decreased and the fatigue life shortened. In conclusion, the heat treatment parameters have an important effect on the microstructure and properties of isothermal quenched ductile iron.

3 CADI research progress

3.1 Origin of CADI and casting method

In 1992 the United States take the lead in the research and development of ADI containing carbide (Carbidic Austempered Ductile Iron, CADI) [14-16], CADI group of graphite ball, carbide and the iron matrix. CADI is a further development of ADI materials. In the production of CADI, a certain amount of carbide is required in the as-cast structure to increase hardness and wear resistance, which is the main difference between CADI and ADI. The carbide morphology in CADI generally presents a continuous network. In the as-cast state, the matrix of CADI is mainly pearlite. After isothermal quenching treatment, the matrix structure changes from pearlite to ferrite. Compared with high chromium cast iron, CADI has higher toughness and lower cost. As a new wear resistant material, CADI has the following advantages : (1) good impact toughness. The impact toughness of non-notched specimens at room temperature is more than 2 times that of wear-resistant cast iron. (2) Good wear resistance. Carbide is dispersed in CADI matrix, which enhances the wear resistance of CADI. (3) Small density. There is a lot of graphite in the matrix, which is obviously lighter than that of cast steel under the same conditions. (4) Low cost. Excellent wear resistance can be obtained by adding only a small amount of alloy. (5) Good shock absorption. The tissue is distributed in a large amount of graphite, which can effectively absorb vibration and reduce noise. CADI smelting and casting methods are as follows: The first method is to add a small amount of alloying elements (such as Nb, V, Mo, Cr, etc.) in ADI to promote carbide precipitation [18-21]. In the second method, cooling iron is added to the casting to improve the cooling speed [17]. The third method is to reduce the amount of graphitized elements (especially Si).The addition of alloying elements can obviously shorten the interval between steady and metastable eutectic temperatures, promote non-equilibrium solidification, and promote the formation of eutectic carbides.

3.2 Research progress of CADI heat treatment

The heat treatment of CADI is similar to that of ADI, isothermal quenching is adopted. The difference is that there are reticular eutectic carbides distributed at grain boundaries in CADI. These eutectic carbides decompose easily during austenitizing, resulting in the increase of carbon content in matrix and alloy, which will affect the thermodynamics and dynamics of austenitizing and bainitizing transformation, and then affect the microstructure and properties of CADI.As can be seen from the microstructure of CADI obtained at different austenitizing temperatures, both ferrite and austenite become thicker and thicker with the increase of austenitizing temperatures. Especially when the temperature exceeds 950°C, carbides will dissolve in the matrix. Likhite et al. [22] showed that a lower austenitizing temperature (900°C) was more conducive to improving the hardness and wear resistance of CADI than 975°C.Han et al. [19] obtained better wear resistance and corrosion resistance by austenitizing Mo carbide nodular cast iron at 900°C+90min.Dakre et al. [23] found that when austenitizing temperature was 900°C, fine carbides were dispersed in CADI matrix.

However, some important scientific questions about CADI microstructure are often neglected, especially the detailed description of microstructure, the formation and growth process of acicular ferrite, and the potential relationship between phases. Eric-cekic et al. [24] studied the isothermal kinetics of Cu-Ni alloyed isothermal quenched ductile iron. The results show that at 350°C, the ADI process window for Cu and Ni alloying is relatively wide, while at 400°C, the ADI process window for isothermal transformation becomes narrower and moves to the left. At 300°C, the process window period of isothermal ADI is narrower and moves to the right. However, nucleation and growth of acicular ferrite in CADI at different isothermal temperatures are rarely reported. In order to solve the problem that CADI network carbides destroy matrix continuity, Professor Fangqiu Zhu of Hefei University of Technology and his research group explored the process of using high temperature pretreatment to improve CADI toughness. It has been proved that fine bainite sheet has excellent comprehensive mechanical properties [25-29], such as nanostructured Bainite steel. These bainites are composed of extremely fine acicular ferrite lath (about 50nm) and residual austenite between them. Due to the uniform microstructure and low residual stress, this bainitic steel has a unique advantage in the application of large mechanical components. However, given the dynamics of bainite formation, the formation of these bainites usually requires holding at lower temperatures for longer periods of time (sometimes up to 10 days or more) or multiple hot rolling prior to bainite transformation [30], which significantly reduces production efficiency. Therefore, the morphology, size and quantity of hard phase carbides and the size of acicular ferrite must be considered comprehensively to achieve CADI impact toughness, hardness and wear resistance at the same time, and the production efficiency should not be reduced.

3.3 Research progress in CADI performance evaluation

Because CADI will be used in the impact corrosion and wear interaction environment, it is very important to evaluate CADI's corrosion and wear performance and how to improve it. It is well known that corrosion and wear are important failure modes of materials. Compared with dry wear conditions, wear under corrosive conditions is more likely to cause rapid failure of materials [31-35].The wear failure of metal materials under corrosive conditions largely depends on the characteristics (composition, thickness) of the corrosion layer formed at the interface of the contact material [36], as well as the wear conditions and the corrosive solution [37-38].Therefore, to reveal the corrosion and wear behavior of metal materials, it is particularly important to study the corrosion layer formed in different corrosion fluids and the surface layer formed under different wear conditions. At present, the evaluation of wear resistance and corrosion resistance of CADI mainly includes the following equipment. Among them, Professor Sun Yufu's research group from Zhengzhou University used ML-100 abrasive wear testing machine to compare the wear resistance of CADI under different components and heat treatment process. Without considering the dry wear condition of impact fatigue, the test machine is simple to operate and the error is small. The research group of Professor Liu Jinhai [24] from Hebei University of Technology evaluated the wear resistance of CADI by using MLS-225 wet sand rubber wheel wear testing machine and MLD-10 abrasive wear testing machine respectively. In particular, MLD-10 testing machine after improvement, can carry out erosion corrosion wear test and impact corrosion wear test. Under the condition of no dynamic load, CADI erosion corrosion wear test can be realized by adjusting slurry concentration, pH value, sand particle size and motor speed. After loading, the wear resistance of CADI under the interaction of impact, corrosion and wear can be quantitatively evaluated by adjusting the load size.

4 Prospects for development

In recent years, CADI has been widely used in the field of wear-resistant materials. Many scientists at home and abroad have studied CADI mainly from the aspects of alloy composition control and heat treatment process optimization, and achieved a lot of research results. But the results of laboratory studies are far from practical applications. Since CADI came into being in 1992, researchers at home and abroad have mainly studied the effects of elements such as chromium, boron, vanadium, niobium, manganese, molybdenum, tungsten and isothermal quenching process on the microstructure, mechanical properties and wear resistance of CADI. In the past, the research focus was on the improvement of CADI production process. Due to the complexity of CADI structure and the short time of its introduction, the problem of low impact toughness has not been effectively solved, and the failure mechanism under the interaction of impact, corrosion and wear remains unclear. Many studies are needed to apply this excellent wear-resistant material to large diameter wet mills.

5 conclusion

In this paper, the problem of insufficient toughness of carbide isothermal quenched ductile iron (CADI) was solved successfully by microalloying and S&A treatment. The matrix structure of CADI was regulated by temperature control treatment, and the influence of austenitizing temperature and isothermal quenching temperature on the properties of CADI was obtained. In addition, the failure mechanism of CADI corrosion wear and impact fatigue was systematically studied.

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