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Characterization and analysis of non-metallic inclusions in Ni42–Fe expansive alloy

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Abstract: Cracks and ruptures always occur during wire drawing process of 42% nickel-iron expansive alloy. In order to study the reasons of these phenomena, a method of metallographic observation in combination with sample electrolysis was used to characterize the non-metallic inclusions in the alloy wire. The results indicate that the inclusions in the alloy are oxidation products during the process of melting. There are single or complex phase inclusions composed of elements such as Al, Si, Ca, Ti, Fe, and O_2. Among them, the macro-inclusions are TiO_2 compound inclusions formed by the adhesion of Al and Si oxides on them. These inclusions are fragile ones with a low strain rate, as well as a rather high hardness, so that they are the main reason that leads to the surface cracks and ruptures in the alloy wires. The analysis has educed that the key point to enhance the product quality is to promote the cleanliness of the melt, control the types and quantity of non-metal inclusions in the alloy.

Key words: non-metallic inclusions; characterization; analysis

1 Introduction

4J43 alloy is 42% nickel-iron binary alloy and one of alloys with controlled expansion. It is mainly used for producing the core material of dumet wire. The 4J43 alloy is copper-clad, oxidized, and then borated. The round wire with diameter of 0.1−0.8 mm and flat wire with cross-sectional diameter from 0.2×0.8 to 0.24×1.0 mm are available. 4J43 expansive alloy put in very high requirements on its surface quality because of particular application of its wire[1]. In recent years, worldwide researches on 4J43 expansive alloy are focusing on the expansion theory. But the investigation of the behavior of non-metallic inclusions in the 4J43 alloy wire are few reported. After the completion of the analysis work in the earlier stage, we found that nonmetallic inclusions have great influence on the quality of alloy products[2].

At present, there are many methods available for analyzing inclusions in alloy[3−9]. However, all the information obtained in connection with inclusions is rather simple due to the respective limitations with each method. The conventional metallographic technique used for examining inclusions is simple, quickly and lower cost. There the optical microscope (OM) is often used to evaluate the inclusion level of alloy products. But its results always have an uncertainty level when the gathering of more precise information on the alloy quality is taken into consideration, such as the size, shape, and chemical composition of nonmetallic inclusions in the alloy. Because the fact that the inclusions in the alloy are randomly distributed and oriented， the possibility to find out the inclusions of all types on a metallographic face is rather little. Even if multiple grindings are done, the observation can merely be made in several planes, and the overall morphologies of inclusions cannot be seen. Therefore, it is hard for a study adopting metallographic detection method to reach a correct and comprehensive conclusion. On the other hand, adopting an electrolytic method[6, 10−12] to extract inclusions can obtain inclusions particles with morphologies similar to those when they are in the steel, and can further

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investigate their physical phase composition. However, this method cannot obtain any information about the distribution conditions of inclusions in the alloy, because the matrix of alloys would then be destroyed.

In order to obtain more precise information，both metallographic examination and electrolytic analysis are applied to investigate the origin of inclusion in this paper. The non-metallic inclusions extracted from 4J43 alloy bar were characterized by using scanning electron microscopy (SEM) in combination with energy spectrum analysis (ESA) and electro probe microanalyzer (EPMA).

2 Experimental

2.1 Preparation of samples

The experimental materials were the 4J43 alloy rod. The analyzed compositions are listed in Table 1.

Table 1 Chemical composition of 4J43 alloy (mass fraction, %)

C	P	S	Si	Mn	Ni	Fe
0.1	0.012	0.012	0.2	1.0	42	Odds

The conventional metallographic samples were processed as shown in Fig.1(a), the sample surface area for observation was about 200 mm^2. The samples were prepared according to the standards GB/T10561－2005 for observation of nonmetallic inclusions.

The electrolytic samples were processed as shown in Fig.1(b). The original rod has a diameter of 12 mm, and it should be processed into a sample with a specification of d10 mm×110 mm. The sample should be drilled and tapped at one of its ends so that it is convenient to lift it during the process of electrolysis. The sample should have a mass of 42.58 g after washed off dirt and oil stains on the surface by applying alcohol and ether.

2.2 Conventional metallographic method

The size, shape, type, and chemical composition of the nonmetallic inclusions are normally characterized by observing metallographic specimen with scanning electron microscopy (SEM) in combination with energy spectrum analysis.

2.3 Electrolytic extract method

The experimental devices are shown in Fig. 2. The electrolytic parameters are as follows: taking the sample and the stainless steel electrolytic bath as the anode and cathode respectively; the current density of the anode being not larger than 100 mA/cm^2. The main components of the electrolytic solution include vitriol, NaCl, complexing agent, and reducing agent with their proportions of 3%, 11%, 0.5%, and 0.5%, respectively. The pH value of the electrolyte is between 5 and 6. During the process of electrolysis, the temperature of the electrolyte and the electrolytic time are controlled in the range of −5 to 5 ℃ and 24 h, respectively.

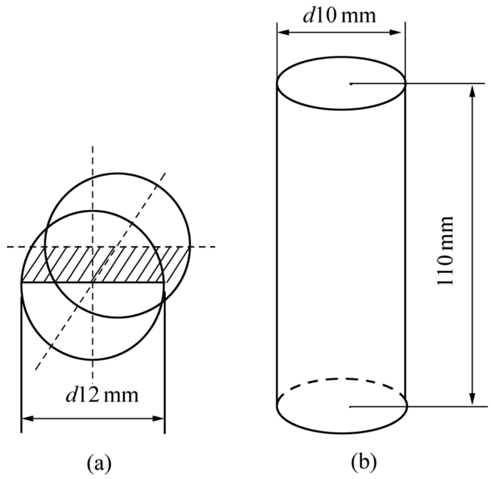

Fig.1 Schematic diagram of sample: (a) Metallographic specimen; (b) Sample electrolyzed

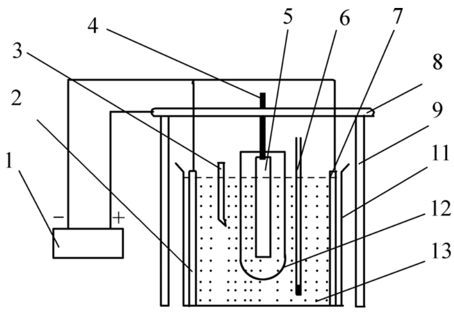

Fig.2 Schematic diagram of electrolytic device: 1—Power supply; 2—Cathode; 3—Calomel electrode; 4—Bolt; 5—Anode; 6—Thermograph; 7—Cathode; 8—Copper bar; 9—Bracket; 10 — Electrobath; 11 — Electrolyte; 12 — Anode chamber

The electrolytic separation course of the nonmetallic inclusions is mainly as follows: sample electrolysis → anode cleaning → elutriation → magnetic separation → washing → drying → weighing. We adopt instrumentations such as the scanning electron microscope (SEM), and electronic probe microanalyzer (EPMA) to analyze the quantity, morphology, size, chemical composition, and microstructure of the nonmetallic inclusions, respectively.

3 Results and discussion

3.1 Result of metallographic method

Fig.3 shows the morphologies of nonmetallic inclusions in the 4J43 alloy obtain by using the scanning electron microscope(SEM). These inclusions vary in size and shapes, and irregularly distribute in the alloy surface and the crack edges.

Fig.4 shows the morphologies of individual inclusions in the 4J43 alloy. Table 2 lists the nonmetallic inclusions elements, being mainly A1, Si, Ca, Ti, and Ni

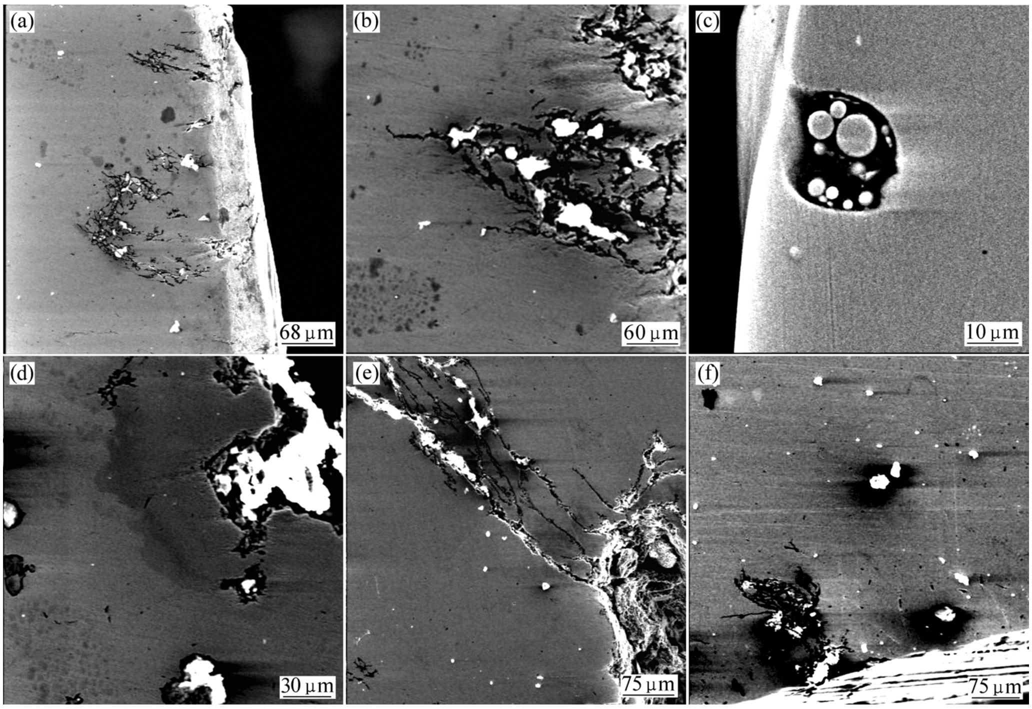

Fig.3 Inclusions around crack and on surface of alloy: (a), (b), (d) and (e) Inclusions around crack; (c), (f): Inclusions on surface of alloy

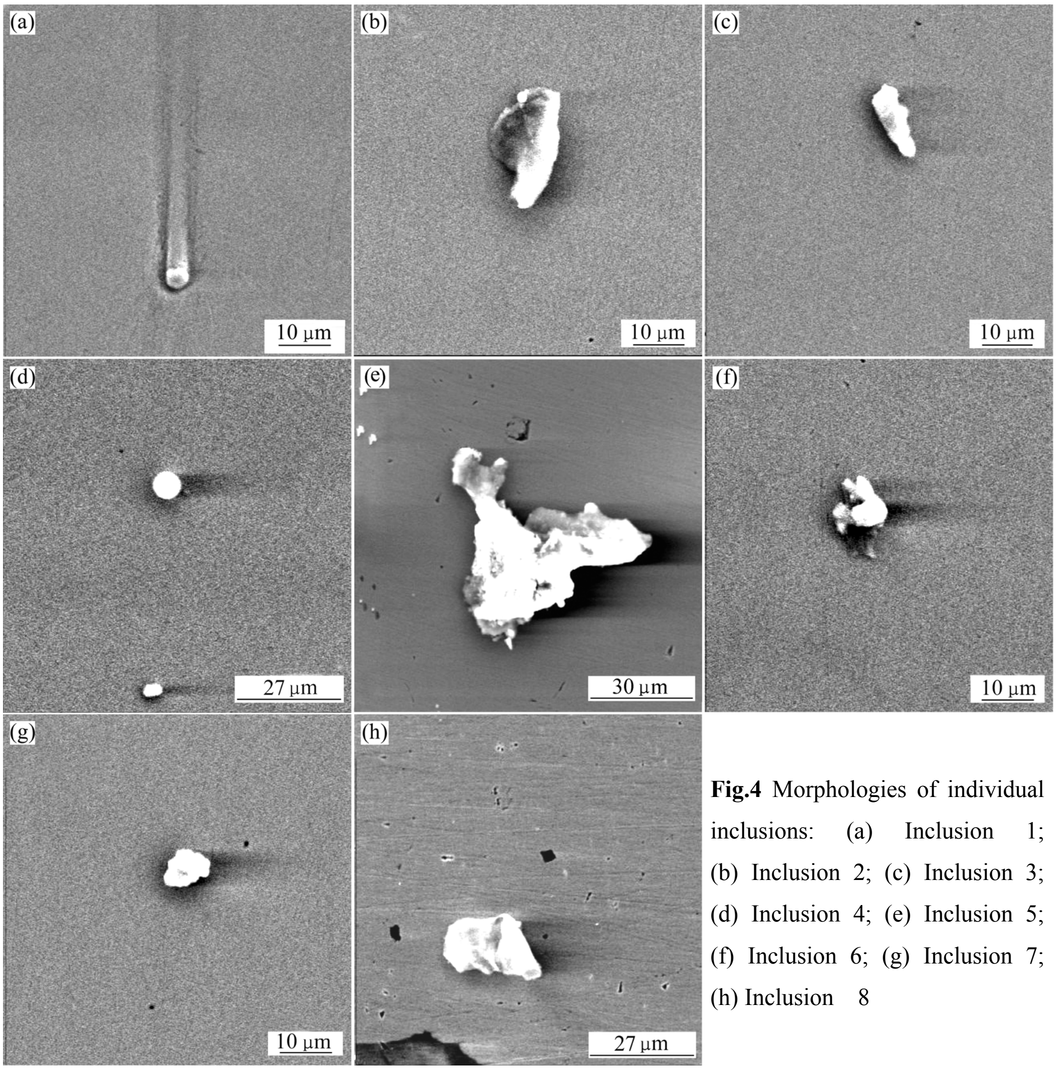

Fig.4 Morphologies of individual inclusions: (a) Inclusion 1; (b) Inclusion 2; (c) Inclusion 3; (d) Inclusion 4; (e) Inclusion 5; (f) Inclusion 6; (g) Inclusion 7; (h) Inclusion 8

Table 2 Chemical composition of inclusions (mass fraction, %)

Inclusion No.	Al	Si	Ca	Mg	S	Ti	Fe	Ni
1	21.89	17.08	32.75				23.78	
2	22.25	27.51				26.32	13.43	10.49
3	24.11	38.73	10.84		17.2		9.16	
4		100.00						
5	23.79	38.63				37.58		
6	42.13	42.58					15.29	
7	24.85	75.15						
8	16.37	25.22	20.11	19.3			19.00	

that is found by using the scanning electron microscopy (SEM) in combination with energy spectrum analysis. Among these inclusions, the round inclusions are mainly A1 oxide and Si oxide, and the irregularly shaped or strip inclusions are mainly A1, Si, Ca, Ti, Ni, Fe, and their compounds, the dimensions of these inclusions are from 1 to 25 μm.

3.2 Result of electrolytic inclusions

3.2.1 Analysis results of inclusions content

The content of inclusions in the 4J43 alloy is shown in Table 3.

Table 3 Content of inclusions in alloy

Mass/g			Content of inclusions in sample/%
Before electrolysis	After electrolysis	Inclusion	
42.584	18.452	0.009	0.0373

3.2.2 Main shapes and composition of inclusions

The scanning electron microscopy (SEM) was used to characterize the three-dimensional morphology and surface features of various inclusions extracted. It is found that the comparatively fine inclusions extracted from the 4J43 alloy with electrolytic method kept their original shapes. As shown in Fig.5, there are several main forms: large regular inclusions with sharp angles (Fig.5(a)); round inclusions (b); small blocks of irregular inclusions with obtuse angles (Figs.5(c)−(d)); regularly triangular or strip inclusions (Figs.5(e)−(f)). Among them, the fist type inclusions have comparatively large dimensions (50−300 μm), while other three types of inclusions possess smaller dimensions, with a large quantity.

The chemical composition of the nonmetallic inclusions was analyzed with scanning electron microscopy (SEM) in combination with energy spectrum analysis, and the result similar to that of the metallographic analysis was obtained as shown in Fig.6(a). The large block inclusions with sharp angles are mainly

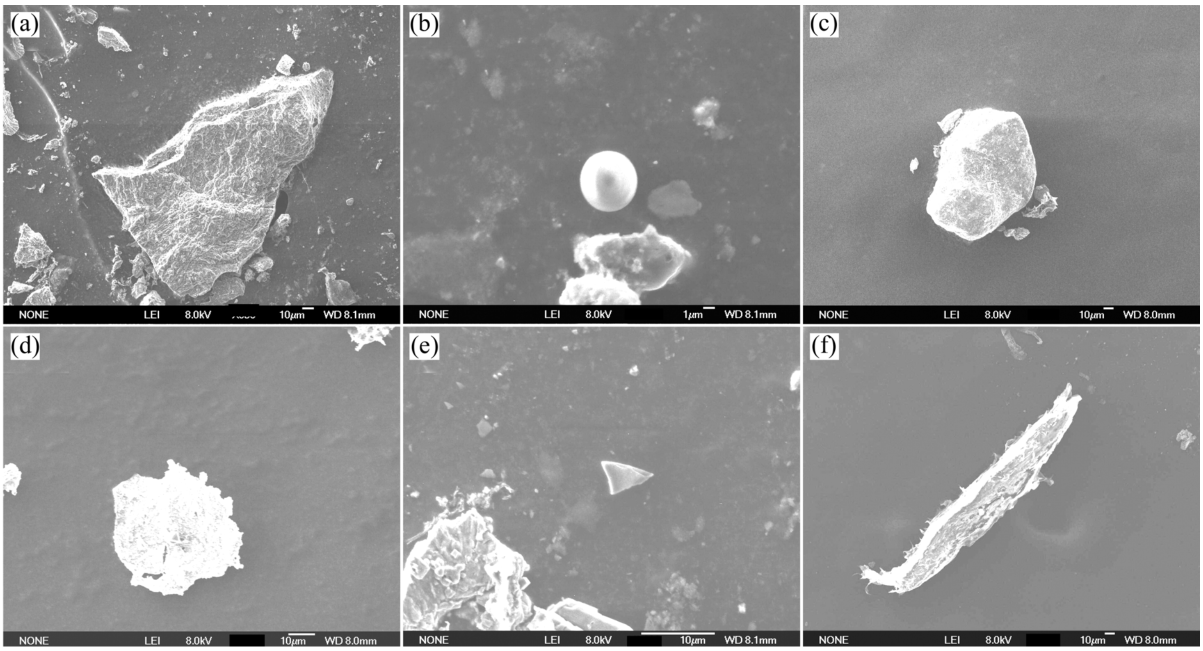

Fig.5 Morphologies of inclusions extracted from alloy with electrolytic method: (a) Larger regular inclusions with sharp angles; (b) Round inclusions; (c), (d) Small blocks of irregular inclusions with obtuse angles; (e), (f) Regularly triangular or strip inclusions

compounds composed of elements such as O_2, Al, Si, S, Ti, and Fe with a respective dimension larger than 50 μm (the maximum of diameter inclusions). In addition, there are lots of small particles adhering to their surfaces. The results of energy spectrum analysis of these particles show that they were mainly oxides composed of Al and Si. As shown in Fig.6(b), the irregular small blocks of inclusions with obtuse angles are composed of O_2, Al, Si, and Fe elements. The inclusions of this type are alumina silicate with main compositions of SiO_2, Al_2O_3, and a little of ferrous oxide as well.

In order to make a further analysis of the microstructure of the large inclusions in the 4J43 alloy, a mapping scanning analysis was performed for the extracted large inclusions by using electro probe microanalyzer (EPMA), and the result similar to that of aforesaid analysis was obtained. These inclusions are composed of elements such as O_2, Al, Si, S, Ti, and Fe. As shown in Fig.7, the morphologies of the large inclusions and the aluminum and ferriferous oxides adhering to the surfaces of the titanium oxides inclusions could be observed clearly.

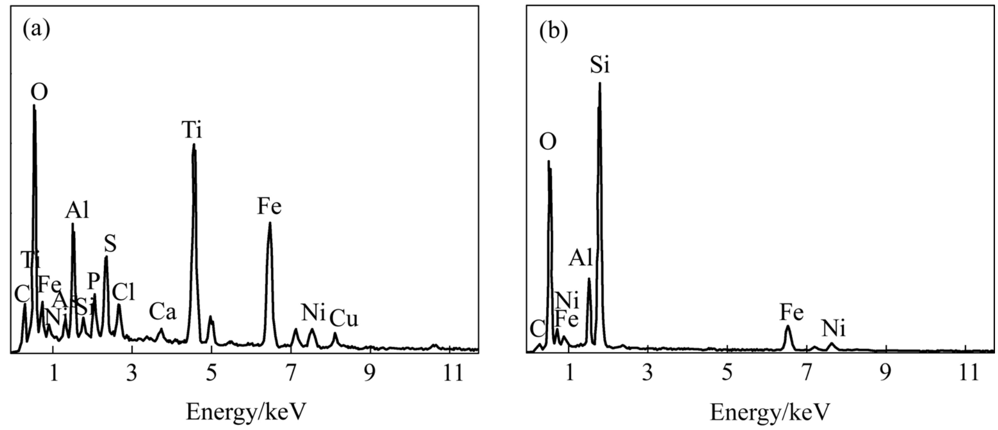

Fig.6 EDS diagrams of inclusions: (a) Macro-inclusions; (b) Micro-inclusions

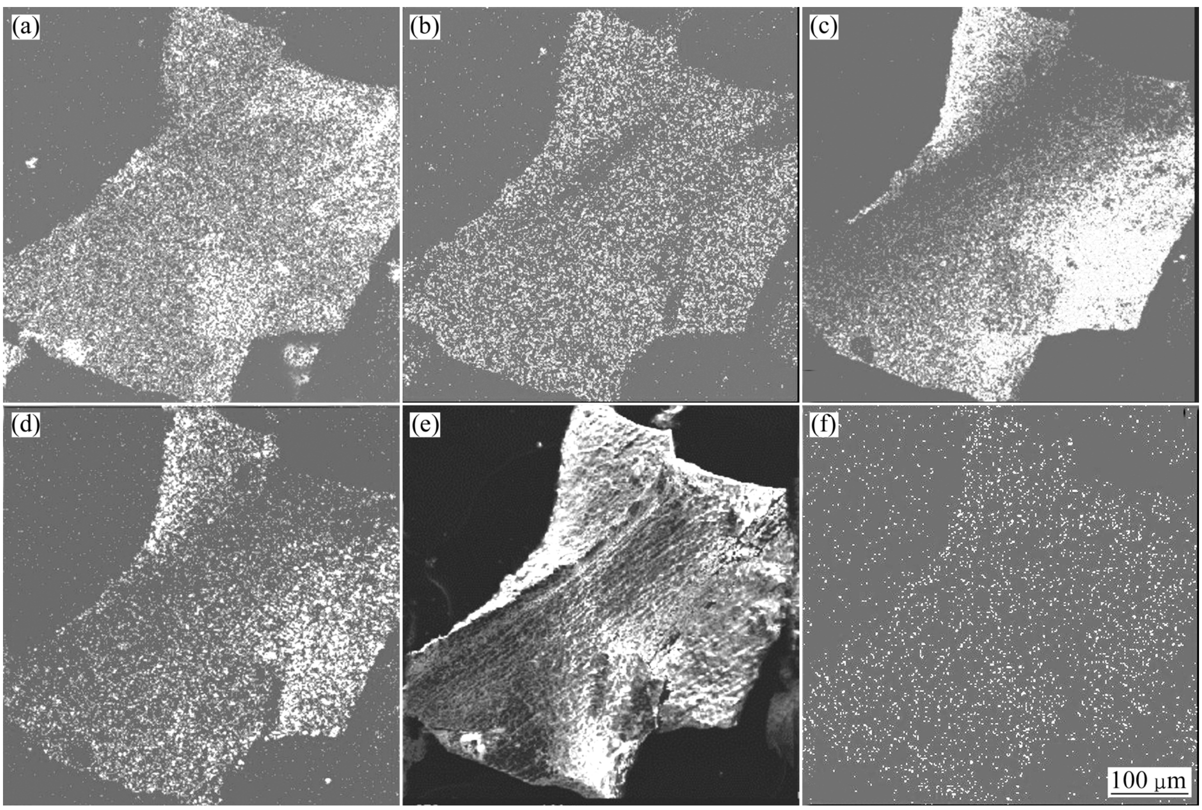

Fig.7 Mapping scanning analysis of elements in large inclusions: (a) Fe; (b) S; (c) Ti; (d) Al; (d) Morphology of inclusions; (f) O

3.3 Origin of inclusions and analysis

Employing the method of metallographic examination in combination with that of electrolytic analysis, it can be accurately analyzed and identified that the inclusions detected from the 4J43 alloy are mainly the deoxidation products generated during the process of melting. All of these products are internal inclusions, nonuniformly distributed within the alloy surface and around the crack edges.

Most of the inclusions are with smaller dimension, round morphology or obtuse angle, which are mainly Al_2O_3, SiO_2, and a little of calcium-silicate. They are the deoxidized products of the aluminum, crystal silicon, and calcium used in the process of smelting as desoxidants. They possess high melting points (1 670 ℃ and 2 050 ℃ for SiO_2 and Al_2O_3 respectively) and high rigidity (HD700 for SiO_2 and HD420-600 for calcium-silicate)[11]. They are fragile inclusions without plasticity. Usually the micro-inclusion is thought of as harmless to the alloy quality. But recent research shows that the fragile inclusions with however small size will affect the alloy anti-fatigue and anti-impact abilities, leading to occurrence of micro-cracks in the alloy products, which has mainly something to do with the volume and quantity of the micro-inclusion.

The large inclusions in the 4J43 alloy are mostly the compound inclusions composed of elements of Ti, Al, and Fe. Most of the inclusions of this type have a square morphology and a dimension larger than 50 μm. They totally account for about 20% of among the inclusions. These larger inclusions are mainly the oxidized products generated from the titanium desoxidant in the process of production. A lot of micro-oxide inclusions composed of the elements Al, Si, and Fe take place during the deoxidizing course, and agglomerate continuously. They can not float up completely due to a shortage of sedation time, so that remained in the alloy melt. These compound inclusions are fragile ones with a low distortion rates and a rather high rigidity, which causes them to easily suffer from cracks and ruptures due to stress concentration during the rolling and pulling of the 4J43 alloy, leading to serious harm of the alloy's quality. The main causes are as follows.

1) Because a rather large difference in deformability between fragile inclusions and alloy matrix, the uniformity and continuity of alloy matrix are destroyed during the processing and deforming process, resulting in stress concentration and micro-cracks at the edge between alloy matrix and inclusions. With increasing strain intensity, the crack extends and macroscopic gap or fracture forms.

2) The compound inclusions possess a larger size and the stress field caused by the inclusions will increase with the size of inclusions. Generally, the cracks would first generate in the interface between larger-sized compound inclusions and alloy matrix. The cracks would propagate along the border of the inclusions till they declutched with matrix of the alloy, causing flaws such as ruts and cracks appear in the surface of the alloy.

3) The compound inclusions possess regular geometry, and some of them have remarkable sharp angle. During the pulling process, the cracks would first generate at the tip of inclusions which are orthogonal to the drawing direction and propagate along the interface between inclusions and alloy matrix, resulting in detachment of the inclusions from the alloy matrix.

It may be known from the above analysis that larger-sized deoxidized products which formed due to Ti, Al, and Fe remained in the alloy are the main cause of crack formation during the rolling and pulling process. In order to improve the alloy product quality, the key point is to improve the cleanliness of the melt, control the types and quantity of non-metal inclusions in the alloy, and optimize the melting, pouring, and refining processes of 4J43 alloy.

4 Conclusions

1) The method of combined metallographic observation and sample electrolytic can be more accurate one for analyzing the amount, shape, dimensions, chemical composition, and distribution of the non-metallic inclusions in the alloy.

2) The inclusions in the 4J43 alloy are deoxidation products in the process of melting, being internal inclusions.

3) Larger-sized deoxidized products of Ti, Al, and Fe remained in the alloy are the main reason of crack and fracture formation during the rolling and pulling process.

4) In order to improve alloy product quality, the key point is to improve the cleanliness of the melt and optimize the refining processes of 4J43 alloy.

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