Study on dispersion of nano ZrO$_2$ particles in pure iron based on high temperature laser confocal

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Abstract
Nano ZrO$_2$ particles were modified and their morphology were analyzed and characterized. The distribution and dispersion of untreated nano ZrO$_2$ particles and pre-dispersed nano ZrO$_2$ particles were compared. Instead of traditional induction heating furnace, physical melting model was constructed by high temperature laser confocal microscope. Pre-dispersed modified nano ZrO$_2$ particles and untreated nano ZrO$_2$ particles were added to the iron powder respectively. The movement and morphology of nanoparticles during solidification of molten steel were observed. Scanning electron microscopy was used to observe the distribution of nanoparticles. Morisita’s index was used to calculate the dispersion uniformity quantitatively. The results show that the untreated nano ZrO$_2$ particles agglomerate at the edge, and it is difficult to exist stably in the metal. The pre-dispersed nano ZrO$_2$ particles are evenly dispersed in molten steel without obvious agglomeration and have better dispersion.

1. Introduction
It is a frontier technology to strengthen the mechanical properties of metal materials by adding second-phase nanoparticles. It is also an easy way to improve strength under current technical conditions. It has important practical significance [1–3]. Nanoparticles are not only different from microscopic atoms and molecular clusters, but also from macroscopic bulk materials. They are metastable intermediate substances between macroscopic solids and molecules. When the particle size enters the nanometer order of magnitude, the ratio of the surface atoms to the total volume atoms increases sharply with the decrease of the particle size, which makes the nanoparticles show strong volume effect, quantum effect, surface effect and macroscopic quantum tunnel effect. Under the combined action of high surface energy, surface electrostatic charge gravity, van der Waals force and chemical bond, the energy of nanoparticles is in an unstable state. So nanoparticles can easily be stabilized by aggregation [2, 4, 5]. According to the Second Phase Reinforcement Theory, when the radius of particles is less than the critical radius, slip displacement dislocation will cut the nanoparticles instead of bypassing them. At this time, the nanoparticles can become the core of external nucleation in the as-cast structure, pinning grain boundaries to prevent grain growth and play the role of grain refinement, thereby improving the strength, toughness and plasticity of metal materials [6]. On the contrary, once agglomerated into secondary particles, impurities will form and affect the quality of steel.

As early as the 1970s, Masayoshi et al [7] used plasma spraying to disperse oxide particles with different proportions to study the change of steel properties during the casting process. The agglomeration of nanoparticles resulted in no obvious strengthening effect. Later, people found a way to solve the agglomeration of nanoparticles. Wang et al [8, 9] improved the uniform dispersion ability of nanoparticles in molten steel by controlling their size and morphology, increased their wettability with the matrix, and achieved surface modification and modification by adsorbing, chemical reaction, coating and film formation on the surface of nanoparticles with modifiers. However, Liu et al [10–12] found it very difficult to characterize nanoparticles, especially their dispersibility. On the one hand, because of the small size of nanoparticles and the very small
amount of nanoparticles, it is difficult to find more difficult to determine their distribution in heavy steel ingots, which is also not conducive to the study of their dispersibility. On the other hand, Lee et al. [13, 14] used equipment such as induction heating furnace to carry out experiments. Such equipment could not be controlled under non-vacuum conditions, such as melting, heating temperature, heating speed and so on. It could not guarantee the repeatability of experiments. The conclusion was contingent. Under such uncertain conditions, it was difficult to characterize nanoparticles in steel or to draw accurate regular conclusions. We found that these uncontrollable conditions can be avoided by using high temperature laser confocal microscopy as melting equipment. Most scholars [15–18] used high temperature laser confocal microscopy to observe the phase transformation and solidification process. Because high temperature laser confocal microscopy can accurately control the melting conditions such as melting temperature, heating rate and cooling rate in vacuum environment, repetitive experiments can be carried out in controllable environment and 3D images can be presented. The melting pattern based on high temperature laser confocal technology is very small. It is helpful for the addition and mixing of nanoparticles in iron powder before smelting, and it is convenient to get the distribution law of nanoparticles, which will promote the study of the distribution and movement law of nanoparticles in molten steel in the future. So the high temperature laser confocal technology was introduced into metallurgical field.

For the above reasons, to prevent the agglomeration of nanoparticles before adding into molten steel, we pre-dispersed nano-ZrO₂ particles and compared them with untreated nano-ZrO₂ particles in terms of dispersion. The physical melting model was built by High Temperature Laser Confocal Microscope. Untreated nano-ZrO₂ particles and pre-dispersed nano-ZrO₂ particles were added to iron powder respectively and melted under the same conditions. The movement and morphology of nanoparticles during solidification of molten steel were observed. Scanning electron microscopy was used to observe the distribution of nanoparticles. Morisita’s index was used to calculate the dispersion uniformity quantitatively.

2. Experimental method

2.1. Pre-dispersion of nano-ZrO₂ particles
Nano-ZrO₂ particles with the size of 20 nm were put into the ball mill for grinding. After 3 h of ball milling, the soft connection between the nano-ZrO₂ particles was opened, and Fe₂O₃ particles with the size of 10 nm were added, the amount of adding was 3 times of the weight of nano-ZrO₂ particles. The materials were mixed slowly in the ball mill. After 2 h of mixing, the ball mill was adjusted to the state of high-energy ball milling, keeping for 72 h. The nano-ZrO₂ particles coated with Fe₂O₃ particles were obtained.

The materials taken out were put into the high-pressure gas-solid reaction furnace, and hydrogen was introduced for closed cycle reaction. The heating temperature of the high-pressure gas-solid reaction bed was controlled to 300 °C, and the pressure of the circulation system was maintained at 0.3 MPa. After 3 h of reaction, the heating power was turned off, and the materials were discharged into the storage tank under sealed condition, and then argon was introduced into the storage tank to reduce to room temperature, and finally the pre-dispersed nano-ZrO₂ particles were obtained, Pre-dispersed treatment Flow chart as shown in figure 1.

2.2. Analysis and characterization of pre-dispersed ZrO₂ particles
The untreated nano-ZrO₂ particles and the pre-dispersed nano-ZrO₂ particles were respectively scanned by SEM. It can be seen from figure 2(a) that the untreated nano-ZrO₂ particles agglomerate due to their high surface energy characteristics. As shown in figure 2(b) the boundary between the pre-dispersed nano-ZrO₂ particles is obvious, without agglomerations, and the particle diameter is about 150 nm.

It can be seen from figure 3 that Zr atom is wrapped in the middle of Fe atom, which reduces the surface energy of Zr particles, increases the wettability with iron-based materials and plays a role of pre dispersion.

It can be seen from figures 3 and 4 that Zr atoms are coated in Fe atoms and separated from each other, so they can not contact with each other and agglomerate before the experiment. The pre-dispersion treatment can...
effectively prevent the agglomeration of zirconia before adding, reduce the difficulty of dispersion, and solve the problem that nano-ZrO$_2$ particles are difficult to disperse uniformly in the molten steel.

2.3. Smelting process
Iron powder was melted by high temperature laser confocal microscopy. Iron powder was put into two aluminium oxide crucibles with a diameter of 6.8 mm. ZrO$_2$ nanoparticles with a mass fraction of 0.5% and ZrO$_2$ nanoparticles with a pre-dispersed content of 0.5% were added to the two samples respectively. High temperature laser confocal microscopy was vacuum pumped three times. Nitrogen was injected as protective gas. Started heating, heating speed was 298 K, iron powder completely melted at 1883 K, maintain this temperature for 30 s, stopped heating, started cooling to room temperature, cooling speed was 283 K.
After smelting, the samples were inlaid with a hot inlaying prototype, roughly and finely ground with metallographic sandpaper, and polished with a polishing machine. After corrosion with 4% nitric acid alcohol solution, the tissue structure was observed under optical microscope. The samples were polished again for scanning electron microscopy (SEM) and hardness test. The distribution of nano-ZrO₂ particles was observed and the grain size was measured.

3. Result and discussion

3.1. Distribution of nanoscale ZrO₂ particles

Figure 5 shows the line scanning image of the specimen under SEM. The line scanning method is to draw a straight line in the field of vision, and then scan the distribution of elements on this line. The wave curves of Fe elements and Zr elements are presented. Comparing with the stationary fluctuations of the Fe elements, the curves of the Zr elements fluctuate greatly, which indicates Zr element existence of the Zr elements on the straight lines in the cast. Figure 5(a) shows the addition of untreated nano-ZrO₂ particles, in which large white spots are added nano-ZrO₂ particles. Particle diameter is about 5 microns. Figure 5(c) Adding pre-dispersed nano-ZrO₂ particles, in which the white spots are pre-dispersed nano-ZrO₂ particles, Particle diameter is about 200 nanometers. It is obvious that The surface shape appearance figure and the line scanning analysis figure show that the existence of Zr elements in the pure iron steel.

Figure 6(a) is the scanning image of the sample with untreated nano-ZrO₂ particles. The nano-ZrO₂ particles were not found in the inner part of the casting, and a few nano-ZrO₂ particles were found at the edge of the casting. It shows that the nano-ZrO₂ particles can not exist in the inner part, only a few particles remain and agglomerate at the edge of the casting. Figure 6(b) is the scanning image of the sample added with modified nano-ZrO₂ particles. The nano-ZrO₂ particles are uniformly dispersed in the casting. It shows that the surface pre-dispersed nano-ZrO₂ particles do not agglomerate obviously in the casting and can exist stably in the casting.

The experimental results show that the untreated nano-ZrO₂ particles are very easy to agglomerate, and have poor dispersibility, they can not exist stably in molten steel. Only a small number of nano-ZrO₂ particles remain in molten steel and agglomerate at the edge of the casting. Because nanoparticles are in a state of energy instability under the combined action of high surface energy, surface electrostatic charge attraction, van der
Waals force between nanoparticles and hydrogen bond, it is easy for nanoparticles to reach a steady state through agglomeration, which is not conducive to the uniform dispersion of nanoparticles in molten steel, the inhomogeneity of dispersion and the sparse retention of nanoparticles \[19\]. Because of the above reasons, the effect of improving the mechanical properties of steel is not obvious, and the purpose of strengthening the mechanical properties of steel can not be achieved \[20\]. So nano-ZrO₂ particles were surface modified. Avoid agglomeration of nano-ZrO₂ particles before adding molten steel, play the role of pre-dispersion and hyper-dispersion. The surface pre-dispersed nano-ZrO₂ particles can be uniformly dispersed in molten steel without obvious agglomeration. Most of the nanoparticles are retained in molten steel. The cutting slip displacement during solidification of the metal structure, and the nano-ZrO₂ particles become the core of external nucleation in the as-cast structure. The grain boundary is pinned to prevent grain growth and refine the grain. The effect of particles can improve the strength, toughness and plasticity of metal materials \[21\].

3.2. Quantitative characterization of dispersion

Field emission scanning electron microscopy (FESEM) was used to magnify the sample by One hundred thousand times. Figure 7(a) was a sample with untreated nano-ZrO₂ particles, and figure 7(b) was a sample with pre-dispersed nano-ZrO₂ particles. According to figure 7(a), no nano-ZrO₂ particles were found in the samples added with untreated nano-ZrO₂ particles (Table 1). Figure 7(b) showed that the pre-dispersed nano-ZrO₂ dispersed evenly without large-scale agglomeration.

The untreated nano-ZrO₂ particles were not found in the castings. We counted the number of nano-ZrO₂ particles to be 0. The surface pre-dispersed nano-ZrO₂ particles were counted in different parts of the castings. Table 2 is the number of modified nano-ZrO₂ particles that are amplified by figure 7(b).

Morisita’s index method can be used to analyze the distribution of individuals in the whole. Calculating the dispersion of nano-ZrO₂ particles in castings by Morisita’s Index. The mathematical expression of the Morisita’s index \(I\) is as follows \(1\) \[22\].

\[
I = \frac{\sum_{i=1}^{n} n_i(n_i - 1)}{M(M - 1)}
\]

In the form, \(P\) is the total number of images used. \(n_i\) is the number of nanoparticles in the \(N\) image. \(M\) is the total number of particles. If \(I < 1\) shows that nano-ZrO₂ particles distribute evenly. The closer to 1, the better the dispersion of nano-ZrO₂ particles. If \(I > 1\), it indicates agglomeration of nano-ZrO₂ particles. The greater the 1, the worse the dispersion.

As shown in table 2, the number of nano-ZrO₂ particles is calculated at random location. Because of the untreated nano-ZrO₂ particles are not found in the casting, Moricia’s index is 0, which indicates that the untreated nano-ZrO₂ particles are not added into the casting, and the untreated nano-ZrO₂ particles do not play the role of second phase strengthening. Morisita’s index \(I\) was used to calculate the dispersion of nanoparticles in castings with nano-ZrO₂ particles modified by surface modification. The \(I\) value is 0, 91. It shows that the nano-ZrO₂ particles are evenly dispersed in the casting.

Because of their unique characteristics and easy reunion. Nano-particles rises in the form of clusters in the process of adding molten steel. It is difficult for nano-ZrO₂ particles to remain in molten steel in steady state. Only a few nanoparticles remain in the edge of the casting. This is why the untreated nanoparticles have little effect in the casting. Due to the special surface modification of nano-ZrO₂ particles, the interaction force on the surface of nano-ZrO₂ particles is reduced, and the degree of agglomeration of nano-ZrO₂ particles is reduced, so...
as to achieve the purpose of pre-dispersion. After surface modification, nano-ZrO₂ particles were evenly distributed in the as-cast structure, Morcia’s index is 0.91. The difference between the numerical value and 1 indicates that the dispersion of nano-ZrO₂ particles is not completely uniform, and we can not accurately control the distribution of nano-ZrO₂ particles in as-cast structure. In the process of surface modification of nanoparticles, the surface of each nanoparticle has not been modified. The above reasons may be related to the failure of Morcia’s index to approach 1, which is also the direction of our future efforts to break through the difficult problems.

4. Conclusion

The distribution of untreated nano-ZrO₂ particles and pre-dispersed nano-ZrO₂ particles on the surface of pure iron were compared. The experimental results were analyzed and the following conclusions were drawn:

Table 1. Addition of ZrO₂ Particles.

| Particles       | Iron powder weight (g) | ZrO₂ weight percentage (wt%) | ZrO₂ powder weight (g) | Gross mass (g) |
|-----------------|------------------------|------------------------------|------------------------|---------------|
| untreated ZrO₂  | 0.4193                 | 0.50                         | 0.0023                 | 0.4216        |
| pre-dispersion  | 0.4235                 | 0.50                         | 0.0023                 | 0.4258        |

Table 2. The number of nanoparticles magnified one hundred thousand times.

| Serial No. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | Total |
|------------|---|---|---|---|---|---|---|---|---|----|-------|
| Particle No.| 5 | 12| 15| 8 | 7 | 11| 9 | 14| 13| 13 | 107   |
1. It is difficult for untreated nano-zirconia particles to be added into liquid metals, and it cannot enhance the mechanical properties of metals by second-phase particles. It is necessary to reprocess nano-particles to reduce surface energy and increase the wettability of their surfaces in order to make nano-particles more uniformly dispersed into metal materials.

2. The untreated nano-ZrO₂ particles agglomerated at the edge of the casting, and no nano-ZrO₂ particles were found in the inner part. Moricia’s index is 0, indicating that the untreated nano-ZrO₂ particles could not be uniformly dispersed in the molten steel and could not play a strengthening role.

3. The surface pre-dispersed nano-ZrO₂ particles can exist stably in the casting structure without obvious agglomeration, and play the role of pre-dispersion and super-diffusion. Moricia’s index is 0.91. It shows that nano-ZrO₂ particles are uniformly dispersed.

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