Modifying of mechanical properties in the deposited metal prepared by welding wire containing nanosized oxide particles

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Abstract
Fine oxide particles can play a role in refining grains and promoting nucleation in steel. In this research, a solid welding wire containing nanosized oxides was obtained by preparing a ‘master alloy’. The oxide size was studied by optical microscopy, scanning electron microscopy and transmission electron microscopy. The results show that micron-sized oxides were crushed into nanosized particles under thermal shock in the welding wire steel smelting process. The mechanical properties of deposited metals were studied by tensile and Charpy impact tests. The results demonstrate that the low-temperature impact toughness of deposited metal is effectively improved by adding oxides to wires. When the oxide content was 1%, the impact absorbed energy was 59 J at −40 °C. Compared with that of the deposited metal without oxides, the impact absorbed energy increased by 22.92%. The addition of oxides refines the original austenite grains and promotes acicular ferrite nucleation so that the deposited metal has better mechanical properties. To obtain good strength toughness matching, the welding wire with 1% oxides has the best comprehensive properties.

1. Introduction
From the perspective of weld design, a weld should meet the plasticity or toughness requirements [1, 2]. In actual production, heat treatment or deformation treatment is generally not required after welding. Solution strengthening seems to be the only way to strengthen welds [3]. With the increase in alloying elements, the weld strength increases, but the toughness decreases. Therefore, in this work, through welding wire made in a special way, nanosized oxide particles are transported into the deposited metal to refine the structure. The deposited metal achieves a good match of strength and toughness.

Many scholars have found that fine oxide inclusions in HSLA welds can refine the structure and promote the formation of acicular ferrite. Cai [4] studied the effect of rare earth yttrium oxide on the weld properties of high-strength steel electrodes. The tensile strength was reported to be as high as 800 MPa. Luo [5] found that nanoparticle clusters appeared in the deposited metal. These clusters vary in size from 1 μm to 1.5 μm. Luo concluded that the nanoparticles might be the titanium oxide particles that were initially added. Beidokhti and Kang Y [6, 7] found that when the titanium content was less than 0.05%, the acicular ferrite content was promoted and the impact toughness was improved.

Hasegawa [8] sprayed oxides and sulfides on molten steel and found that steel had higher strength and better thermal stability; however, their methods can only produce 10 kg ingots. In this work, during the smelting and remelting of the ‘master alloy’, the micron-sized oxides were fragmented and distributed evenly in the welding wire. The present work avoids the problems of floating, agglomeration and uneven distribution caused by directly adding nanosized oxides to the molten steel, more importantly, can achieve the effect of mass production.
2. Materials and methods

2.1. Preparation of materials

To study the effect of nanosized oxide particles on the microstructures and mechanical properties of the deposited metal, two different contents of Al$_2$O$_3$ + TiO$_2$ were added to the welding wire: #2 wire and #3 wire were added to 1% and 2% Al$_2$O$_3$ + TiO$_2$, respectively. The #1 wire (Al$_2$O$_3$ + TiO$_2$ 0%) was the control group.

In the present experiment, the production process of welding wires was as follows. First, industrial alumina ($\gamma$-Al$_2$O$_3$), titanium powder (rutile-TiO$_2$), silica powder and boron oxide were weighed at a mass ratio of 40:40:10:10, mixed and milled to a particle size of 0.1 $\mu$m to 10 $\mu$m. Second, they were mixed with 20 steel (in GB standard) particles at a mass ratio of 1:9. Third, the mixtures heated to 1500 °C were cast into moulds after maintaining the temperature for 2 h. Through the above process, a ‘master alloy’ with oxide particles homogeneously distributed in the steel was made. Using the ‘master alloy’ as raw materials supplemented by other raw materials, three types of experimental steels were made. After forging, rolling, and drawing, solid welding wires with a diameter of 1.2 mm were finally made. The chemical compositions of the welding wires are shown in Table 1.

The oxide particles in the welding wire steel were electrolytically extracted in an aqueous solution of 1 wt% NaCl, 2 wt% citric acid and 3 wt% FeSO$_4$. The current values vary from 0.05 ~ 0.1 A cm$^{-2}$, and the pH value varies from 2 to 3. After drying, the Fe$_3$C particles in the extracted products were removed by a magnet. The residual extracted products were employed for further analysis. In figure 1, Q235 (GB 700–2006) was used for the test board (250 mm × 100 mm × 20 mm) and backing board (250 mm × 25 mm × 6 mm). Multilayer and multipass welding was used, and the welding parameters were shown in Table 2. X-ray inspection showed that the weld was flawless.

2.2. Material characterization

Observation of inclusions was performed with optical microscopy at a magnification of 100×. The oxides in the steel were analysed by scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS). The extracted products were fished for by copper grids and observed with transmission electron microscopy (TEM). The austenite grain boundaries were etched with FeCl$_3$ solution after mechanical grinding and polishing. The

![Figure 1. Schematic diagram of welding.](image-url)

Table 1. Chemical composition of welding wires (wt%).

| Wires | C  | S  | Mn | Si | P  | Cr  | Ni  | Mo | Ti  | B  | O  |
|-------|----|----|----|----|----|-----|-----|----|-----|----|----|
| #1    | 0.100 | 0.008 | 1.75 | 0.63 | 0.015 | 0.40 | 2.33 | 0.660 | 0.022 | 0.0011 | 0.0005 |
| #2    | 0.108 | 0.001 | 1.80 | 0.33 | 0.013 | 0.40 | 2.30 | 0.621 | 0.030 | 0.0014 | 0.0009 |
| #3    | 0.107 | 0.002 | 1.69 | 0.23 | 0.009 | 0.39 | 2.25 | 0.596 | 0.050 | 0.0014 | 0.0012 |

Table 2. Welding parameters used in experiments.

| Shielding gas (%) | Gas flow Q/(l·min$^{-1}$) | Welding speed V/(cm·min$^{-1}$) | Welding Current I/A | Welding Voltage U/V | Interlayer Temperature T/°C |
|-------------------|--------------------------|-----------------------------|------------------|------------------|-------------------------|
| 80Ar+20CO$_2$     | 20                        | 40                           | 270              | 29               | 150                     |
prior austenite grain boundaries were observed by optical microscopy (OM). Metallographic specimens were cut from the centre of the weld and etched with 4% nital solution after mechanical grinding and polishing. The microstructures of the deposited metals were observed using SEM.

After preparing the standard specimens (GB 39281-2020), tensile testing was performed on a universal testing machine at a loading speed of 2 mm min⁻¹. The size of the impact sample was prepared according to GB 229-227. The Charpy impact test was carried out at −20 °C and −40 °C by a JBD-300S impact testing machine. The chemical compositions of the deposited metals were determined with an optical emission spectrometer.

3. Results and discussion

3.1. Microstructures

Figure 2 shows the distribution of oxides in #1, #2 and #3 welding wire steel. Contrary to traditional beliefs, the large-particle oxides introduced by the ‘master alloy’ do not cause more inclusions in the wire steel. We can preliminarily show that during the smelting of welding wire steel, the oxide particles are fragmented.

Figure 3 illustrates the distribution of inclusions in the ‘master alloy’. Because the oxides are nonmetallic, their conductivity is poor, so they appear as white particles in SEM. The energy spectrum analysis proves that the oxide composition is consistent with that of Al₂O₃ and TiO₂ added to the ‘master alloy’, which indicates that these white particles are oxides. As evident in figure 3(a), the size of oxide particles in the ‘master alloy’ is approximately 3 ~ 5 μm (marked by a white circle), and although these particles vary in size, they do not agglomerate and are almost spherical in shape.

To analyse the particle size and distribution of the oxide in the welding wire, the inclusions in the welding wire were observed with a scanning electron microscope.

Figures 4(c), (d) show that these white particles are all added oxide particles, but their sizes are very different from those of oxide particles in the ‘master alloy’. It is known that oxides have poor thermal conductivity, so they easily break under thermal shock. Therefore, many inclusions smaller than 1 micron are observed in the welding wire. Most of the oxide particles are shattered into several smaller particles. Only oxide particles smaller than 1 μm can become strengthening phases in materials [9, 10].

It is difficult to make TEM samples from wires; therefore, oxide particles were electrolytically extracted from the welding wire steel. From figure 5, round or elliptical particles are observed, and the particles vary in size from 50 nm to 100 nm.
From the EDS results of the particles, it is confirmed that the particles are TiO$_2$ and Al$_2$O$_3$. By calculation, the mass fraction of oxides in the ‘master alloy’ is less than ten percent, and the density of the ‘master alloy’ is very close to that of steel. Therefore, the process of preparing intermediate alloys can effectively prevent the uneven distribution of oxide particles in welding wire steel. The oxide particles are broken due to the action of molten steel. This is the reason for the appearance of nanoscale oxide particles in welding wire steel. Fine titanium and
aluminium oxides were introduced into the deposited metal by using welding wires, which greatly refined the microstructures of the weld metal.

Grain refinement is an effective way to increase both the strength and toughness of steel [11, 12]. In figure 6, #1, #2, and #3 correspond to the deposited metal with 0%, 1%, and 2% oxide addition, respectively. Figure 6 shows the prior austenite grain boundaries of deposited metals with different oxide contents. With the addition of 1% oxide, the prior austenitic grains are refined. However, compared with the control group, with the addition of 2% oxide, the austenite grains were not refined. Thus, the addition of oxide particles can indeed refine the microstructure, but with the addition of excessive oxides, this effect is weakened.

As seen in figure 7, the microstructure of the #1 sample is mainly granular bainite (GB), martensite (M) and degenerate upper bainite (DUB). The microstructure of the #2 sample is acicular ferrites (AF) and DUB, and GB is evenly distributed between the bainite slats. Obvious partitioning phenomena can be seen in a primitive austenite grain, and the boundaries of each partition are clear. The area where the laths are in the same direction and the laths are parallel to each other is called a bainite cluster. The bainite lath bundles in the grains are narrower, and their orientation is more obvious. Compared with #2, the bainitic ferrite (BF) laths in the #3 microstructure are coarser.

Figure 8(a) demonstrates that the addition of oxides can form acicular ferrites in the weld metals. Through elemental analysis of the selected area, as presented in figure 8(b), a Mn-poor area is found around the inclusions that induced AF nucleation, which is also an influential explanation for AF nucleation [13–15]. In fact, acicular ferrite has high toughness. Since the growth of AF occurs in multiple directions, with the nucleation of AF, prior austenitic grains can be divided into several small parts [16, 17].

Lan [18] concluded that the range of inclusion sizes is approximately 0.45 ~ 1 μm. Lee [19] found that an inclusion diameter of 0.25 ~ 0.8 μm is beneficial to promote AF nucleation. Compared with the #2 deposited metal, the amount of AF in the #3 deposited metal is much less than that in #2. Under the same welding parameters, the finer inclusions in the #2 deposited metal seem to be more beneficial to promoting acicular ferrite formation. From figure 9, Image-Pro software was employed to count the size of inclusions in the #2 and #3 deposited metal. With the addition of 1% oxide, inclusions with a size of 0.2 ~ 0.6 μm accounted for 61%, and the size of the inclusions was within the range needed to effectively promote the formation of AF. With the addition of 2% oxide, inclusions with a size of 0.2 ~ 0.6 μm accounted for 30%. In figure 10, large inclusions appear in the #3 deposited metal; moreover, some of them debond from the matrix. The energy spectrum results show that the large inclusions may form from the agglomeration of oxides.
Figure 8. Typical inclusions induce AF nucleation of the #2 deposited metal.

Figure 9. Distribution and size of inclusions in deposited metals: (a) and (c) #2; (b) and (d) #3.

Figure 10. (a) and (b) Debonding of large inclusions from the matrix in the #3 deposited metal; (c) shows the EDS result of points A in (b).
3.2. Properties

The chemical composition of the deposited metals is shown in Table 3. The oxygen content in the weld increased due to the effect of the protecting gas.

To further understand the mechanical properties of the deposited metals, tensile tests and impact tests were conducted. The tables and figure 11 present the test results. It is very obvious that the impact values obtained for the three samples exhibit a large difference. The impact toughness of the deposited metal with 1% oxide added is the highest, which is consistent with its fine structure. Compared with that of the #1 sample, the control group, the impact absorbed energy increased by 22.92% at −40 °C. Unfortunately, the impact absorbed energy of the #3 sample is the lowest, at 32 J.

Many scholars have studied the structural characteristics of deposited metal with strengths above 690 MPa [20–22]. The interlaced multiphase microstructure composed of different bainites and acicular ferrite can allow welded deposited metal to achieve good strength–toughness matching. With AF acting as the toughening phase and B and M acting as the strengthening phase [23], a multiphase microstructure is formed in the #2 deposited metal, which can explain the relatively high impact toughness of the #2 deposited metal.

![Figure 11. Mechanical properties of deposited metals: (a) stress-strain curves; (b) strength; (c) elongation (A%) and rate of the percentage reduction area (Z%); and (d) impact absorbed energy.](https://example.com/figure11.png)

| Table 3. Chemical composition of deposited metals (wt%). |
|-----------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Numbering | C     | S     | Mn    | Si    | P     | Cr    | Ni    | Mo    | Ti    | B     | O     |
| #1        | 0.101 | 0.009 | 1.46  | 0.48  | 0.015 | 0.38  | 2.23  | 0.620 | 0.020 | 0.0007| 0.0510|
| #2        | 0.120 | 0.003 | 1.48  | 0.20  | 0.013 | 0.40  | 2.21  | 0.620 | 0.030 | 0.0009| 0.0530|
| #3        | 0.120 | 0.002 | 1.53  | 0.28  | 0.015 | 0.49  | 2.45  | 0.620 | 0.050 | 0.0007| 0.0630|

| Table 4. Performance test results of the deposited metal. |
|-----------|-------|-------|-------|-------|-------|-------|-------|-------|
| Numbering | $A_{KV}(-20\text{ °C})/J$ | $A_{KV}(-40\text{ °C})/J$ | $R_{m}$ | $R_{0.2}$ |
| test results | AVE | test results | AVE | test results | AVE |
| #1 | 53, 54, 56 | 54 | 47, 50, 46 | 48 | 1012 | 941 |
| #2 | 64, 68, 69 | 67 | 54, 64, 58 | 59 | 1003 | 931 |
| #3 | 34, 37, 39 | 36 | 28, 34, 33 | 32 | 1030 | 938 |
Remarkably, due to the large amount of oxide added in sample #3, during the cooling process of the weld, the fine oxide particles gradually agglomerated into large inclusions [5]. As a result, these oxide particles lost their ability to refine the structure and turned into a source of cracks that are unfavorable to toughness [24, 25]. This is also the reason why the low-temperature impact toughness of the #3 deposited metal decreased significantly. On the other hand, figures 10(a), (b) shows that these larger inclusions are likely to fall off the matrix and form larger holes, which may cause stress concentration and become the source of cracks.

4. Conclusions

(1) Welding wires with oxides sizes of less than 100 nm were prepared by a special method. The prior austenite grain boundaries of the deposited metal with 1% oxides were refined. Compared with that of the deposited metal with 2% oxides, the smaller size of the inclusions in the deposited metal with 1% oxides results in a higher fraction of acicular ferrite.

(2) The deposited metals of the three wires showed different levels of impact toughness. The Charpy V-notch impact absorbed energy at −40 °C increased from 32 J to 59 J. The comprehensive mechanical properties of the welding wire with 1% oxides were considered the best.

(3) Good matching of strength and toughness could be obtained by the deposited metal forming an interlaced multiphase microstructure, with degenerated upper bainite and martensite acting as strengthening phases and acicular ferrite acting as the toughening phase.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Statement

The data of this study is openly available.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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