Oxidation characterization of M2 powders exposed under humid atmosphere for a long time

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Abstract. Atomized M2 powders were stored in an atmosphere of 80% relative humidity for a long time. The oxidation characteristics of atomized alloy powders were analyzed. The results show that the oxygen content of the powders have an increasing trend with the prolongation of storage time under humid atmosphere. The oxygen content of 150-300 mesh coarse powder has a gentle change, and the oxygen content will be reduced to near the original level after drying. The oxygen content of -300 mesh fine powders has a little growth in a short time, but it increases rapidly as time goes on after one week, and increases from 415 ppm to 1098 ppm after four weeks of storage, and the oxygen content of fine powders after drying remained unchanged. Particle size has a great influence on the oxidation characteristics of powders. The smaller the particle size, the greater the oxygen content of the powder. The type of adsorption of oxygen element from coarse powder to fine powder changes from physical adsorption to chemical adsorption.

1. Introduction
M2 die steel is a molybdenum tool steel with a domestic grade of 6542, which has advantages of small carbide non-uniformity, high strength and toughness. Due to its hardness and wear resistance, it is often used to make superior cutting tools. It is also commonly used to make molds suitable for vibration and impact loads, such as cold forging dies, precision stamping dies, powder compacting dies, and metal cutting. Saw blades, cold heading and extrusion tools. Studies related to the wear resistance of M2 steel are quite a lot [1-4], as it is still the quite popular material in the field of tool steel.

It is still dominated by imported products in the field of high-end tool steel in China. Because of the high alloy content, high-end tool steel is mainly prepared by powder metallurgy. Rapid manufacturing technologies including 3D printing, thermal spraying, and spray forming, which are now the important topics, are all in the category of powder metallurgy.

Non-metallic defects frequently prevent the full performance potential of structural materials from being realized, which can be seen not only in traditional manufacturing technologies, but also in additive manufacturing technologies [5, 6]. Inclusion-type defects are typically composed of non-metallic compounds such as nitrides, oxides, etc.. But the source of non-metallic compounds may be different when we use different manufacturing technologies.
It can be seen from the principle of powder metallurgy that the quality of raw material powder used is a key factor, which has directly related to the stability of the process and the quality of molding, so the powder quality becomes the most important part of the industrial chain and an important part of the process technology. The basic and most important requirement of powders is high purity, including low oxygen content of the powder, and no non-metallic inclusions.

As discussed above, the quality of the powder has a critical impact on the quality and performance of the product in the field of additive manufacturing. When there is too much gas content in the powder, especially oxygen, which will tend to form an oxide film at the boundary of the powder during laser cladding, 3D printing or powder metallurgy consolidating, leading to a significantly degradation of the performance of the powder product [7-11]. The metal powder with a low oxygen content can be obtained by an inert gas atomization method, but there is a possibility of contamination of a gas such as oxygen during the post-treatment of the powder, which has a negative effect on the purity of the powder. Powder post-treatment processing is an important part of the preparation process of powder products. The process mainly includes the steps of sieving treatment of the powder, vacuum degassing treatment, storage, and so on. Among them, the screening of powders, especially vacuum degassing, a lot of work has been done at home and abroad, also a great progress has been obtained [12, 13].

However, there is little work related to the storage of alloy powders, and there is also lack of systematic and comprehensive research. A suitable powder storage method, especially during the long-distance transportation, has a great influence on effectively reducing the oxygenation of the powders during the post-treatment process and ensuring its purity. In this paper, the metal powders were prepared by inert gas atomization method, and the sieved powders was stored in a humid environment. The effect of storage time and powder characteristics on the oxygen content of the powders was studied, and the oxidation characteristics of the powders were also analyzed. The experimental and theoretical basis for improving the post-treatment process of powders, especially the storage environment.

2. Experiment process
The M2 steel powders used in this work were prepared by argon atomization and the two kinds of powder particles were used after sieved, which size contribution is 0-50 μm and 50-150 μm separately. Its chemical composition is C 0.9 %, Si 0.38 %, W 6.2 %, Cr 4.1 %, Mo 4.8 %, V 2.1 %, Fe Bal. Both powder samples were stored in an environment with a relative humidity of approximately 80% for 3, 7, 14 and 28 days, respectively.

After storing for different time, the powders were taken out, part of the trays containing the samples was placed in a blast drying oven and dried at a temperature of 120 °C for two hours, then they were vacuum packaged.

Oxygen and nitrogen analyzers were used to track the oxygen content of the powders after storage for different time and corresponding drying. And X-ray diffraction (XRD) technique has been used on samples using a Bruker Da Vinci with Cu Kα radiation in a 2θ range from 5° to 95°.

Figure 1. The powder of M2 steels atomized by argon
3. Results and discussion
The morphology of the alloy powder is shown in Figure 1. It can be seen from the figure that the particles of the argon atomization powder are mostly sphericity, and the size of the powder particles is substantially distributed between 0 and 100 μm after preliminary screening. The two distribution regions in which powder particles’ size is more concentrated are about 10-20 μm and 50-80 μm, respectively. Larger particles have satellite spheres and cladding on the surface; while smaller particles are mostly smoother spheres. At the same quality, the number of particles of the fine powder is much larger than the number of particles of the coarse powder; also the surface area of the fine powder is also nearly five times that of the coarse powder.

![Figure 2](image)

**Figure 2.** Oxygen content of humid and dried powder particles VS storing time

(a) fine powder particles, (b) coarse powder particles

3.1. Effect of storing time on the oxygen content of powders
Figure 2 shows the variation of the oxygen content of the alloy powder with storage time under a humid environment. It can be seen from the curves in the figure that the oxygen content of the powders increases with the storage time under the humid environment, and the oxygen content curve of the 150-300 mesh coarse powder particles is more flat, as stored for 4 weeks, the oxygen content increased from 276 ppm to 480 ppm, and the oxygen content decreased to 339 ppm after dried, indicating that oxygen content of the dried powders after storing for a long time under a humid environment will be reduced to the original level, which can be used as usual; But to fine powder particles (-300 mesh), the oxygen content of the powders does not change much in a short time, while after one week, the oxygen content grows faster with time, increases from the initial 415 ppm to 1098 ppm after four weeks of storage. The oxygen content of the dried powder still does not change much.

For the iron-based alloy of M2, the oxidative corrosion when stored in air is strongly affected by the moisture content in the air. When the relative humidity in the air reaches 80%, it is close to the second critical relative humidity of the iron-based alloy [14], at which time the oxidation rate of the powder increases rapidly with the increase of the relative humidity in the air. From the oxidation kinetic analysis, it is known that due to the low oxygen content of the original powder, a very dense oxide film is not formed on the surface of the powder particle, and the initial stage of oxidation follows a straight line law, the oxygen content increases at a steady rate. As the oxidation process proceeding, the oxide layer at the surface of the powder particles acts as a strong oxidant in a humid environment, causing an accelerated increase in oxidation rate [14]. The fine powder, due to the larger specific surface area, makes the weight gain curve of oxidation closer to the power exponential function; it can be seen in Fig. 2.

When a water film is adsorbed on the surface of the powder particles, a corrosion reaction as shown as following:

Anode

\[
\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^-  
\]
Cathode

\[ \text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O} \quad (2) \]

The produced ion Fe\(^{2+}\) exists in the form of hydrated ions in the solution, and the reaction formula is as follows:

\[ \text{Fe}^{2+} + \text{H}_2\text{O} \rightarrow \text{FeOH}^+ + \text{H}^+ \quad (3) \]

The corrosive intermediate FeOH\(^+\) can be rapidly oxidized by \text{O}_2 to form FeOOH [15, 16], so FeOOH accumulates on the surface of the powder to form an early rust layer. The reaction formula is as follows:

\[ 2\text{FeOH}^+ + \text{O}_2 + 2e^- \rightarrow 2\text{FeOOH} \quad (4) \]

By studying the atmospheric corrosion of steel, some scholars [17] believe that FeOOH, which is in direct contact with the metal matrix or connected by the electrical conductor, will undergo a reduction reaction, thereby aggravating the corrosion of the matrix. The reduction reaction can be expressed by the following formula:

\[ 3\text{FeOOH} + \text{H}^+ + e^- \rightarrow \text{Fe}_3\text{O}_4 + 2\text{H}_2\text{O} \quad (5) \]

**Figure 3.** XRD patterns of fine powder samples storing for different times under humid atmosphere and as-dried sample

XRD analysis was performed on fine powders stored in a humid environment for different times, as shown in Figure 3. The measurement results show that the FeOOH phase and the Fe\(_3\)O\(_4\) phase are present after the fine powder stored for one week. The diffraction intensity of the FeOOH phase changes little with the extension of the storing time, while the intensity of the diffraction peak of the Fe\(_3\)O\(_4\) phase increases continuously, which indicates that the FeOOH layer (outer rust layer) in the humid atmosphere can promote the corrosion of the M2 steel powder, and also FeOOH can be reduced to participate in the cathode reaction. It can be seen that when stored in an 80% humidity environment for a long period of time, the fine powder will undergo a reduction reaction as shown in the above formula.

Although the corrosive intermediate product can be continuously converted into FeOOH, there is not much FeOOH in the rust layer due to its reduction, so the rust layer which starts to corrode is very thin. At the same time, Fe\(_3\)O\(_4\) produced by the reduction of FeOOH will accumulate between the rust layer and the metal boundary, so that the black rust layer is formed rapidly under the initial rust layer, and the inner rust layer (Fe\(_3\)O\(_4\)) is continuously thickened.

Kamimura et al. [18] considered that Fe\(_3\)O\(_4\) has good electrical conductivity and can accelerate metal corrosion as a cathode. Syed [19] believes that Fe\(_3\)O\(_4\) is large particles, and the Fe\(_3\)O\(_4\) layer is
inclined to be loose and porous, which is very beneficial to the transmission of Fe$^{2+}$ and electrons, so the progress of corrosion is accelerated. Sun and Evans [20,21] confirmed that although the oxygen diffusion process is hindered by the Fe$_3$O$_4$ layer, Fe$^{2+}$ and electrons can penetrate the Fe$_3$O$_4$ layer, and the cathode reaction will shift to the surface of the inner rust layer. The experimental results also show that the rust layer can significantly accelerate the corrosion of the fine powder of M2 steel, which can also be inferred that oxygen can be directly reduced on the surface of the inner layer.

Therefore, in the humid environment, the anode reaction of the fine powders still occurs at the interface between the rust layer and the metal, but the cathode reaction is transferred to the surface of the inner rust layer. Since Fe$^{2+}$ and electrons generated by the anode reaction can penetrate the inner rust layer and are oxidized on the surface, FeOOH can be continuously converted from FeOH$^+$ at the interface of the outer rust layer/inner rust layer. However, due to the reduction of FeOOH, the outer rust layer (FeOOH layer) is always thin, while the inner rust layer (Fe$_3$O$_4$ layer) is continuously thickened. Due to the reduction reaction of FeOOH and the cathodic action of the Fe$_3$O$_4$ layer, the corrosion rate of the fine powder will be greatly accelerated.

3.2. Effect of powder particle size on the oxygen content
The particle size of the powders has a direct effect on the oxygen content of the powders. The smaller the particle size of the powders, the larger their surface area which has a greater ability to adsorb the surface of the gas, so the fine powders will have a higher oxygen content. The original oxygen content of the -300 mesh powders is greater than the oxygen content of the 150-300 mesh powders. When stored in a humid environment, the oxygen content of the fine powders increases as a parabolic type curve, while the oxygen content growth curve of the coarse powder is a linear type. From the relative curves of the wet and dry curves, it can be seen that the adsorption of oxygen and water vapor by the coarse powder is physical adsorption, and most of the gas (water vapor) can be separated after drying; the adsorption of oxygen and water vapor by the fine powder belongs to chemical adsorption. After drying, the oxygen content is basically unchanged.

4. Conclusion
M2 powders were prepared by argon atomization method, and the sieved powders were stored in an atmosphere of relative humidity of 80%. The influence of storage time and powder particle size on the oxygen content of the powders was studied, and oxidation characteristics of the aerosolized powders was analyzed. The following is the conclusion:

1. With the prolongation of storage time, the oxygen content of the powders shows an increasing trend. The oxygen content of fine powders has a more pronounced increase. The fine particle powder of -300 mesh has a faster increase in oxygen content over time and increased from the initial 415 ppm to 1098 ppm after four weeks of storage.

2. The drying process has a noteworthy effect on the coarse powders. After four weeks storage, the oxygen content of the coarse powders increases from 276 ppm to 480 ppm, while the oxygen content decreases to 339 ppm after drying. That indicates that the coarse powders being stored for a long time in a humid environment, the oxygen content will decrease to near the initial level after dried, which will not affect its usage; however, the effect of drying on the fine powder after dampness is not notable, which indicates that the oxygen element adsorption mode changed mainly from physical adsorption to chemical adsorption when the powder particle size changed from coarse fine.

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