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LETTER

Mechanism Analysis of Influence of Sulfur Content on Tensile Properties of C71500 Cu-Ni Alloy

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Abstract: Six kinds of Cu-Ni alloys with different sulfur contents were investigated at room temperature for tensile properties. The effects of tensile rate and sulfur content on the yield strength, tensile strength, elongation, and reduction of area of the alloys were studied. The changes of metallographic structure with sulfur content were studied by scanning electron microscope (SEM), energy disperse spectroscopy (EDS) and metallographic structure analysis. The distribution and deformation of sulfur precipitate and the influence law for the plasticity of Cu-Ni alloy were analyzed. The origin and occurrence of alloy fracture process and the influence mechanism of sulfur content on plasticity were analyzed, providing a theoretical basis for subsequent cold deformation process.

Key words: sulfur content; Cu-Ni alloy; tensile property; analysis

In iron-based and nickel-based alloys, sulfur, as a harmful element, must be strictly controlled[1,2]. Qayyum et al[2] studied the 16MnCr5 alloy steel with the addition of sulfur and found that the machinability of alloy improves, but the formability reduces. Zhou[3] studied the effect of sulfur on the thermoplasticity of Ni-Cr-W-Al super alloy and found that with the increase of sulfur content, the thermoplasticity of this alloy decreases continuously, and the sulfur is enriched at the grain boundary with high content. Sawada[4] studied the grain boundary brittleness caused by the grain boundary segregation of Ni and S in fcc-structured iron through the first principle calculation method. Dong et al[5] found that sulfur has a negative effect on the durability, plasticity and hot tensile plasticity of Inconel 718 alloy. Lv et al[6] found that with the increase of sulfur content, the zero ductility temperature and plasticity temperature range of austenitic steel with high manganese content decrease significantly.

However, there are few relevant literatures about the influence of sulfur on copper alloy and Cu-Ni alloy. In this research, the effect of sulfur on the tensile properties of C71500 Cu-Ni alloy was studied. The composition of sulfide and its failure mechanism to properties were investigated. According to different standards, the Cu-Ni alloys with different sulfur contents were developed. Through the tensile test, the influence of sulfur on the structure, properties and processing technique of Cu-Ni alloy was analyzed, providing a theoretical basis for the reasonable control of sulfur content in the Cu-Ni alloy, which is conducive to the optimization of subsequent cold deformation process for Cu-Ni alloy.

1 Experiment

According to GB/T 8890-2015 "Seamless copper alloy tube for condenser and heat-exchanger", the maximum sulfur content of C71500 Cu-Ni alloy should be less than 0.01wt%. According to ASTM-B111/B111M-18a "Standard Specification for Copper and Copper-Alloy Seamless Condenser Tubes

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and Ferrule Stock", if the product is for the subsequent welding applications, the maximum sulfur content is 0.02wt%. According to EN 12451-2012 "Copper and Copper Alloys-Seamless, Round Tubes for Heat Exchangers", the maximum sulfur content of C71500 Cu-Ni alloy is 0.05wt% , and if the product is for subsequent welding applications, the maximum sulfur content is 0.02wt%. Therefore, six kinds of C71500 Cu-Ni alloys with different sulfur contents were prepared. The sulfur content was controlled at <0.0003wt% , 0.0063wt% , 0.0179wt% , 0.0383wt% , 0.0648wt%, and 0.0784wt%. To eliminate the influence of carbon and oxygen, the contents of carbon and oxygen were controlled below 0.001wt%.

Tensile test specimens with diameter of 5 mm cut along the longitudinal direction of forged plates were used, according to ASTM B11 for specific dimensions. The test temperature was 23±5 °C, and the constant true strain rates were 0.0001, 0.001, 0.01 and 0.1 s^{-1}. With the fixed deformation temperature and deformation rate, the fracture and microstructure of the alloy were observed by metallographic microscope and scanning electron microscope (SEM).

The original structure of the Cu-Ni alloy is a single phase equiaxed crystal structure, as shown in Fig.1a. There are a lot of coherent twin boundaries in the microstructure with low sulfur content[7-9]. With the increase of sulfur content, the grain size in the microstructure becomes smaller, the grain boundary changes from straight or planar to serrated, and the number of non-metallic inclusions in the microstructure increases significantly after hot forging. The non-metallic inclusions are mainly distributed at the junction of grain boundaries, and a small number of non-metallic inclusions are relatively dispersed at the grain boundaries.

2 Results and Discussion

2.1 Mechanical property analysis

Fig. 2 shows various mechanical properties of C71500 alloys with different sulfur contents at different true strain rates. It can be seen from Fig.2a that the yield strength of the alloy is relatively low when the sulfur content is less than 0.0003wt% , which is 225.03~250.16 MPa. As the sulfur content increases, the yield strength of the alloy increases rapidly. When the sulfur content increases to 0.0063wt%, the yield strength of the alloy increases rapidly to 288.26~297.14 MPa. At low strain rates (0.0001 and 0.001 s^{-1}), the yield strength of the alloy increases steadily with the increase of sulfur content. When the strain rate increases further, the yield strength of the alloy fluctuates, but the fluctuation does not affect the overall changing trend. With the increase of strain rate, the increment of yield strength of alloy is between 0 and 40 MPa.

It can be seen from Fig.2b that the tensile strength of Cu-Ni alloy with sulfur content <0.0003wt% is very low (365.04~385.75 MPa). The tensile strength of the alloy increases significantly after adding sulfur, indicating that sulfur element is conducive to improving the alloy strength. When the sulfur content increases to 0.0063wt%, the tensile strength of the alloy increases rapidly to 392.06~407.14 MPa. However, when the sulfur content is 0.01wt%~0.04wt%, there is a cold strength groove in the alloy, and the alloy strength rapidly reduces to 385.53~399.39 MPa. When the sulfur content continues to increase, the alloy strength slowly reduces, and the tensile strength of the alloy increases with the increase of strain rate. The increment of tensile strength for alloy at different strain rates is 0~20 MPa.

The elongation of sulfur-containing and sulfur-free Cu-Ni

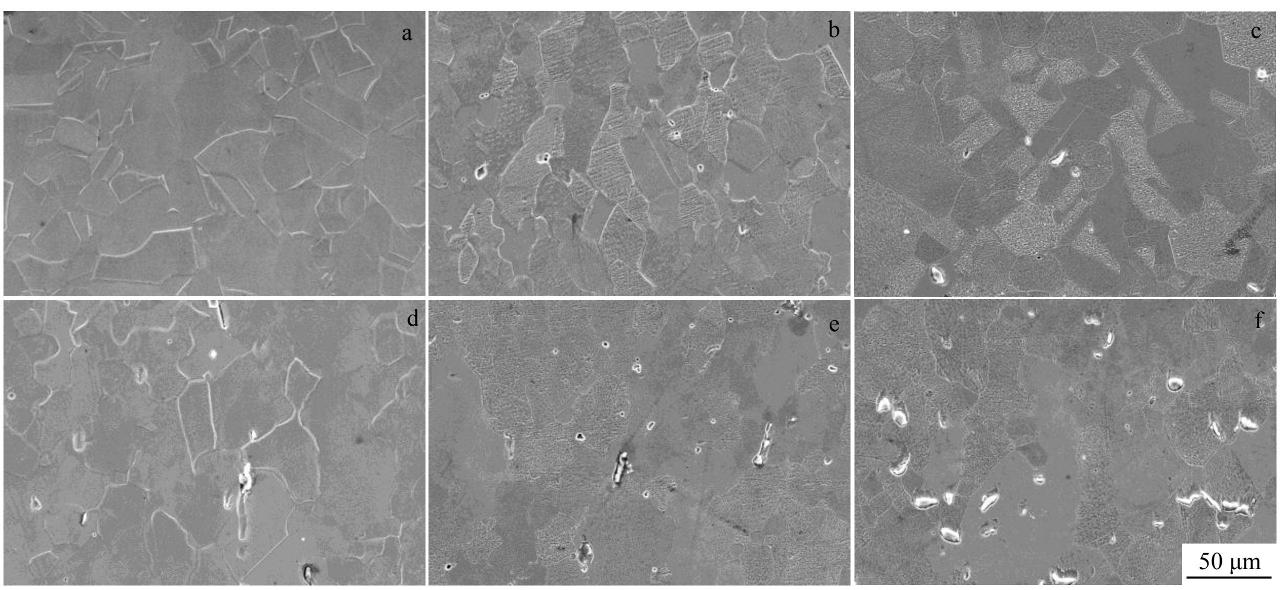

Fig.1 SEM images of Cu-Ni alloys with different sulfur contents at forged state: (a) 0wt%, (b) 0.0063wt%, (c) 0.0179wt%, (d) 0.0383wt%, (e) 0.0648wt%, and (f) 0.0784wt%

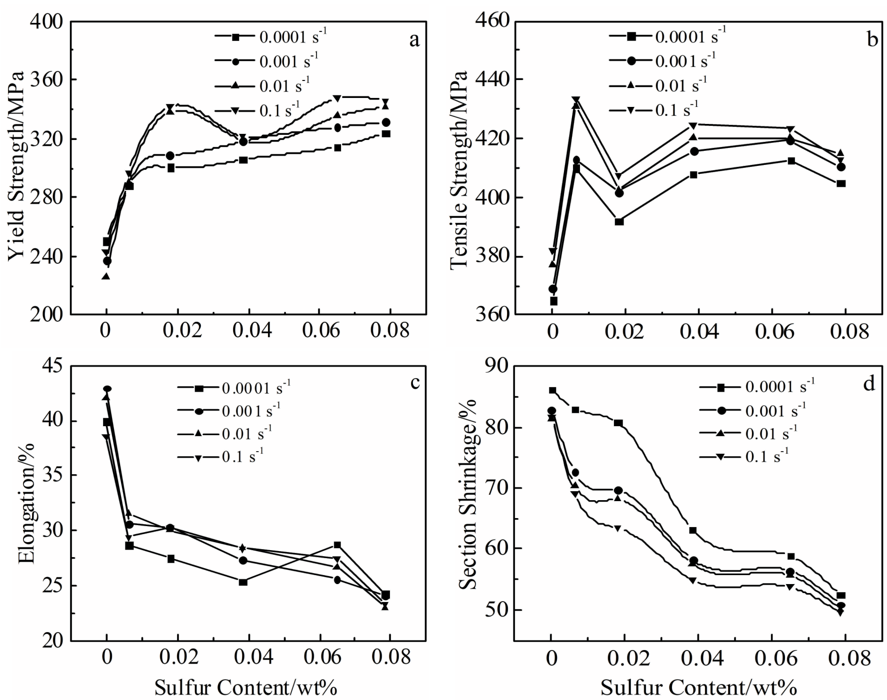

Fig.2 Mechanical properties of alloys with different sulfur contents at different true strain rates: (a) yield strength, (b) tensile strength, (c) elongation, and (d) section shrinkage

alloys is very different. As shown in Fig.2c, the elongation of the alloy decreases sharply after the addition of sulfur element. With the increase of sulfur content, the elongation of the alloy shows an overall downward trend. However, under the condition of high strain rate of 0.1 s^{-1} and low strain rate of 0.0001 s^{-1}, the changing trend fluctuates greatly. In Fig.2d, it can be seen that with the increase of sulfur content, the area shrinkage of the alloy decreases gradually. With the increase of deformation rate, the reduction of material area decreases gradually.

2.2 Fracture morphology analysis

It can be seen from Fig.3 that as the sulfur content increases, the dimple size at the fracture surface of alloy becomes smaller and smaller. The dimple at the fracture of alloy with

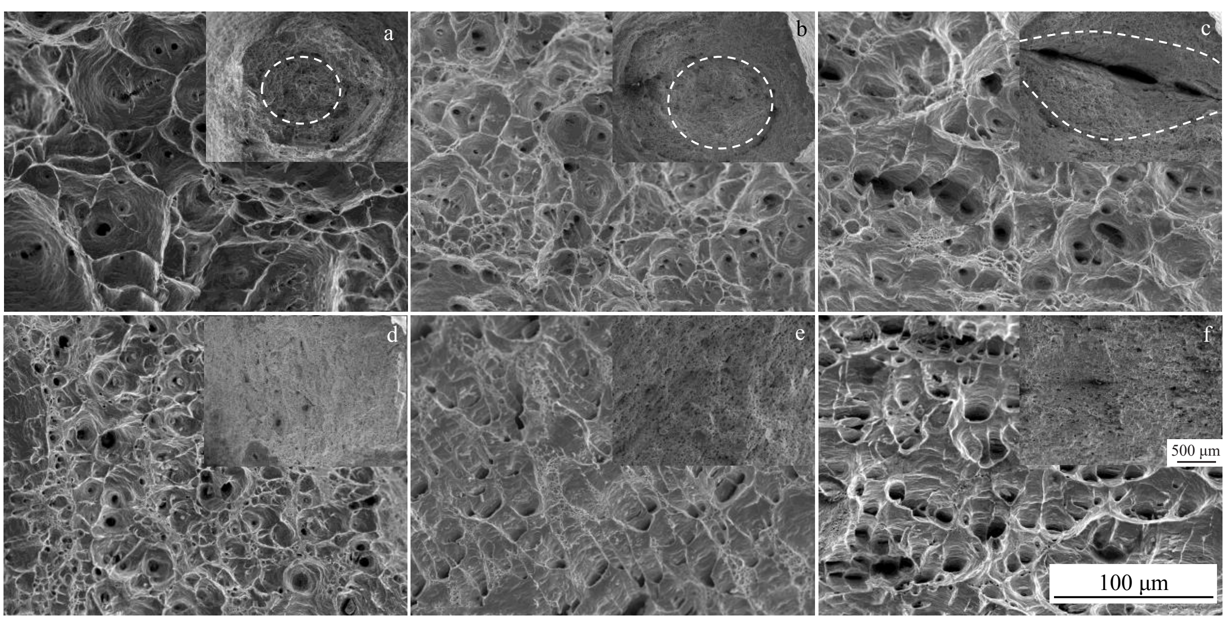

Fig.3 SEM images of fracture morphology of alloys with different sulfur contents at deformation rate of 0.0001 s^{-1}: (a) 0wt%, (b) 0.0063wt%, (c) 0.0179wt%, (d) 0.0383wt%, (e) 0.0648wt%, and (f) 0.0784wt%

sulfur content <0.0003wt% in Fig. 3a is large and deep, and there is almost no non-metallic inclusion at the bottom of the dimple. The macro morphology of the whole fracture resembles a bowl. The fractures with the similar size are basically parallel, and the tearing ridges at the dimple are high and clear (the parts beyond the dotted line in Fig.3). When the sulfur content reaches 0.0063wt%, as shown in Fig. 3b, the macro morphology of the fracture changes: the fracture center is not smooth and flat; some steps occur; the dimples at the fracture become smaller; a few non-metallic inclusions appear at the bottom of individual dimples. With the increase of sulfur content, delamination, shear tearing, and other phenomena are gradually observed on the fracture surface. At the bottom of the dimple, the number of non-metallic inclusions continues to increase, and the dimple size becomes smaller. When the sulfur content of specimen exceeds 0.02wt%, the shear lip structure at the fracture surface of the tensile specimen gradually disappears, and a cleavage platform appears at the fracture surface, indicating that the plasticity of specimen gradually deteriorates, and the macro morphology of the fracture also changes from dimple-like to tear-like shape.

It can be seen from Fig.4 that after deformation, the grain structure of the tensile fracture changes from equiaxed crystal state to fibrous elongated grain along the tensile direction. It is indicated that the material matrix undergoes large plastic deformation, and that there are a large number of micro holes at the place where sulfide is precipitated. With the increase of sulfur content, the micro holes at the fracture of specimen gradually increase in number. Meanwhile, the micro pores mainly form due to sulfur compounds. The compound shows no obvious plastic deformation at room temperature. As the deformation process increases, the binding force between matrix and precipitate gradually breaks, thus forming the micro holes. The stress concentration is easy to form around the micro holes, so the stress on the cross section of specimen is not uniform, further damaging the uniform deformation of the alloy. The specimen of sulfur content <0.0003wt% shows uniform deformation, and the grains gradually elongate along the direction of tensile stress with the increase of deformation, forming fracture dimples. The fracture deformation is at the necking state. When the stress concentration around the local sulfide is greater than the tensile strength of specimens, the specimens with sulfide crack at the local area firstly, and then the cracks gradually expand along the parts with greater stress, resulting in the delamination in Fig.4c and the fracture state of shear tear in Fig.4d~4f.

2.3 Qualitative analysis of precipitates

From the sulfide morphology at the bottom of fracture dimple, it can be seen that there are a large number of sulfide inclusions in the fracture dimple, which are broken in the deformation process, indicating that the inclusions show no plastic deformation at room temperature. The effect of sulfide on the metal matrix and the fragmentation state of sulfide after deformation can be more macroscopically observed through the longitudinal section morphology of specimen, as shown in Fig.5. It can be found that the composition of sulfide inclusion is Mn, Fe, Ni, Cu, and S. By quantitative analysis, the atomic percentage of S is equal to the total atomic percentage of Mn, Fe, and Ni. Therefore, the compound can be named as (Mn, Fe, Ni)S.

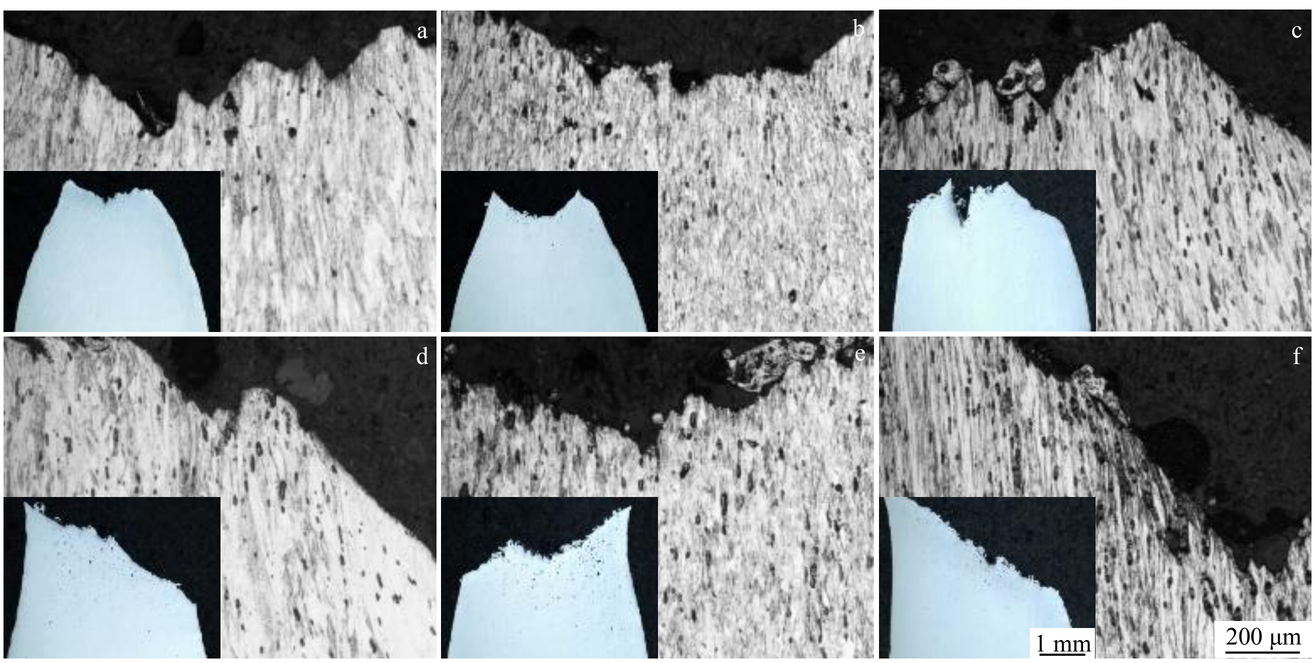

Fig.4 Metallographic morphologies of longitudinal section of fracture for alloys with different sulfur contents at deformation rate of 0.0001 s^{-1}: (a) 0wt%, (b) 0.0063wt%, (c) 0.0179wt%, (d) 0.0383wt%, (e) 0.0648wt%, and (f) 0.0784wt%

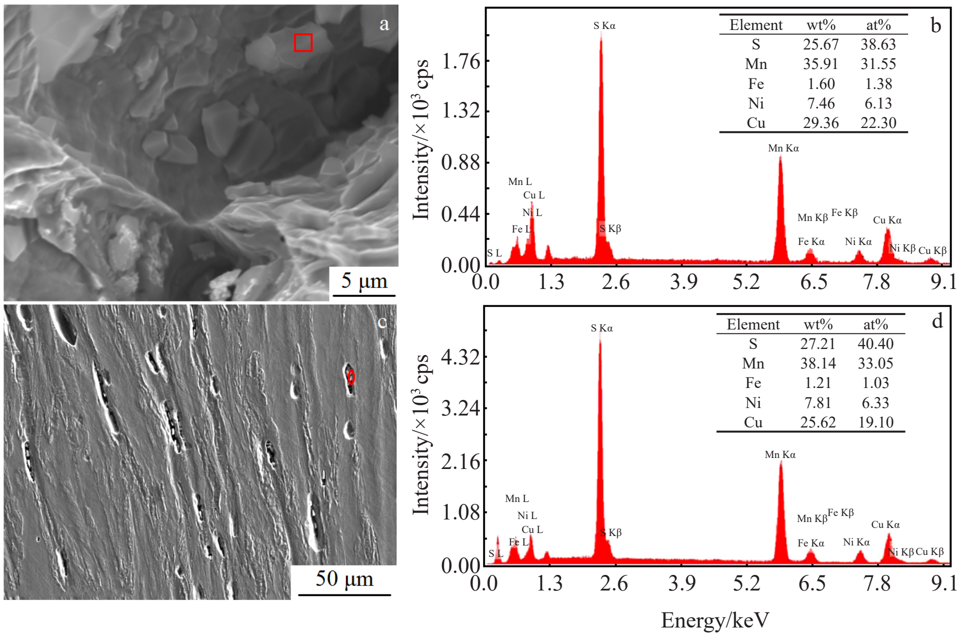

Fig.5 Transverse (a, b) and longitudinal (c, d) SEM images (a, c) and EDS analyses (b, d) of alloy with sulfur content of 0.0784wt%

3 Conclusions

1) With the increase of deformation rate, the tensile strength and yield strength of the C71500 Cu-Ni alloy increase, while the plasticity decreases.

2) The addition of sulfur improves the alloy strength, but the plastic failure of the alloy is evident. The reason for the decrease of plasticity is that the sulfur-containing compounds (Mn, Fe, Ni)S show no plasticity at room temperature and form micro pores after crushing, thus leading to stress concentration and uneven distribution of stress.

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硫含量对Cu-Ni合金拉伸性能影响的机理分析

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摘 要：对6种不同硫含量的Cu-Ni合金进行了室温拉伸试验。系统地研究了拉伸速率和硫含量对材料屈服强度、拉伸强度、伸长率和断面收缩率的影响。通过扫描电镜、能谱分析和金相组织分析，研究了硫含量对金相组织的影响。分析了Cu-Ni合金中硫析出物的分布、变形及对塑性的影响规律。分析了材料发生断裂的起源和过程及硫含量对塑性影响的根本原因，为后续冷变形过程提供理论依据。

关键词：硫含量；铜镍合金；拉伸性能；分析

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