Materials and Design 157 (2018) 469–477

Contents lists available at ScienceDirect

Materials and Design

journal homepage: www.elsevier.com/locate/matdes

Deformation-induced dissolution of copper precipitation in 1.5wt% Cu-bearing antibacterial Fe-17wt%Cr alloy during plastic deformation process

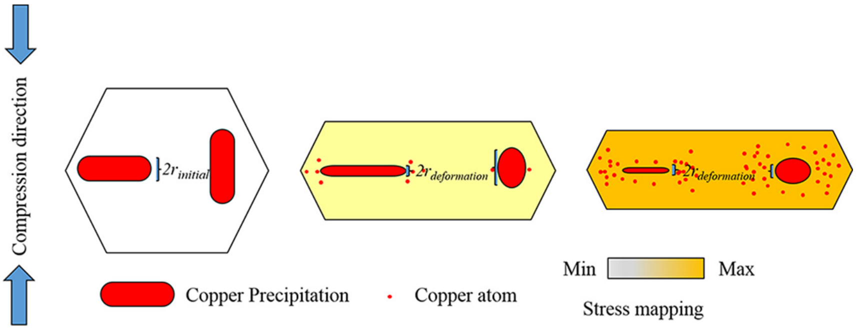
Shaoheng Sun [a,b], Fei Yin [b], Yifei Liu [a], Wei Zhang [c], Aimin Zhao [a,*], Qingyou Han [b]

[a] *Collaborative Innovation Center of steel Technology, University of Science and Technology Beijing, Beijing 100083, PR China*
[b] *School of Engineering Technology, Purdue University, West Lafayette, IN 47907, USA*
[c] *Technology Center of Taiyuan Iron and Steel Coporation, Taiyuan 030003, China*

HIGHLIGHTS

- The copper precipitation dissolved into the matrix during plastic deformation process.
- Severe plastic deformation resulted in deterioration of antimicrobial property.
- The matrix solubility increased and the critical radius of the precipitation decreased during cold rolling process.
- Two dissolution models were proposed based on the arrangement of copper precipitation.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 8 May 2018
Received in revised form 31 July 2018
Accepted 2 August 2018
Available online 06 August 2018

Keywords:
Copper precipitation
Deformation
Dissolution
Antibacterial Fe-17wt%Cr alloy

ABSTRACT

Antibacterial Fe-Cr alloy is emerging in biomaterials. To study the influence of plastic strain on the copper precipitations in this material, a series of experiments were performed in this paper. A commonly used Fe-17wt%Cr alloy with 1.5wt%Cu was cold rolled with a reduction from 12.5% to 75%. It was found that the rod-shaped copper precipitations transformed to acicular or equiaxed and the lattice constant of the matrix became larger after cold rolling which demonstrated that the copper precipitations dissolved into the matrix. The antibacterial tests indicated that the material will lose its antibacterial effectiveness after cold rolling. These phenomena are because that the copper precipitation is softer than the matrix and the plastic deformation more easily occurs in copper precipitation, which significantly improves the gibbs free energy of copper precipitation resulting in a bigger copper solubility and critical precipitation radius. Therefore, the copper precipitation dissolves into the matrix during the cold rolling process and the antibacterial function deteriorates. These results will provide fundamental guidelines for the optimal design of antibacterial Fe-17wt%Cr alloy production process.

1. Introduction

With the rapid development of society, antibacterial materials have been regarded to reduce the risk of infection and further enhance the healing quality [1]. Though the silver can give the antibacterial function to traditional materials [2], the usage of Ag-bearing Fe-Cr alloys is limited owing to the high-cost. During the nineteen nineties, Fe-17wt%Cr-1.5wt%Cu with an excellent antibacterial function was first used in Japan, and Fe-0.3 wt%C-13 wt%Cr-3 wt%Cu and Fe-18 wt%Cr-9 wt%Ni-3.8 wt%Cu soon followed [3]. Cu-bearing antibacterial Fe-Cr alloy is a novel class of structure/function integrated materials developed in

---

* Corresponding author.
E-mail address: aimin.zhao@ustb.edu.cn (A. Zhao).

https://doi.org/10.1016/j.matdes.2018.08.014
0264-1275/© 2018 Published by Elsevier Ltd.

recent years for the low stack cost and excellent mechanical [4–6]. The reason why it can obtain the antibacterial function is Cu^{2+} which can kill *Escherichia coli and Staphylococcus aureus* [7,8]. And Cu^{2+} is known not to be cytotoxic at low concentrations and can enhance bone density for human beings [9,10]. However, the Cu element solid solution into the matrix can't receive the antibacterial function unless it precipitates out as copper precipitation (ε-Cu, FCC structure [11,12]) and grows to a certain size [13,14], otherwise the copper precipitation will be covered by the passive film.

So far, most production processes for the antibacterial Fe-Cr alloys in laboratory employ cold rolling, solution annealing and then antibacterial annealing, which can guarantee there is enough copper precipitation to obtain an excellent antibacterial function [5,15–18]. But, in order to obtain a high quality surface, the process preferred in factory is solution annealing, antibacterial annealing, cold rolling and then recrystallization annealing. The key issue in this process is the effect of plastic strain on the antibacterial function. In other words, the key issue is the effect of plastic strain on the copper precipitation. There have been few studies to examine the Fe-Cr alloy with cold rolling after antibacterial annealing.

Z.X. Zhang et al. [5] have studied the effects of light pre-deformation on the antibacterial rate of copper-bearing Fe-17wt%Cr alloy. After light cold rolling and antibacterial annealing, the size of copper precipitation and antibacterial rate decrease with the increase of cold rolling reduction. But the mechanism has not been discussed in depth. Tsuchiyama et al. [19] have indicated that 35 nm diameter nearly spherical ε-Cu particles are initially elongated along the rolling direction by cold rolling in Fe-2wt%Cu alloy, and then they were partly dissolved into the matrix as the equivalent strain increased. But the dissolution process of the rod-shaped precipitation and the effect of the rod-shaped morphology were not analyzed. Sauvage et al. [20] examined the plastic deformation leading to the dissolution of Cu clusters exhibited in a cold drawn pearlitic steel containing 0.7 at.%Cu. However, the dissolution mechanism was not discussed. Asano found that severe wire drawing resulted in the near complete solution of Cu and the dissolution of Cu particles was quantitatively estimated by electrical resistivity measurements with consideration of the effect of densities of dislocations and strain-induced grain boundaries [21]. While, the systematic explanation was not given from the view of thermodynamics. Donghua Xu et al. [22] have demonstrated that the copper precipitation will re-dissolve into the matrix and proposed a kinetics model in an ion irradiated and thermally annealed Fe-0.78 at.%Cu alloy.

In order to research the effect of cold rolling on the antibacterial function and the position of antibacterial annealing in the whole manufacturing process, it is very necessary to study the effect of deformation on the copper precipitation. Compared with the previous works, the morphology and microstructure evolutions of copper precipitation during heavy cold-rolling were investigated by using an over-aged bearing 1.5wt%Cu Fe-17wt%Cr alloy, in which copper precipitations were with fully grown and uniformly dispersed in the matrix. And then, the change of the matrix lattice constant was studied to research the effect of deformation on the antibacterial function, which proved that the copper precipitations dissolved into the matrix. From the view of thermodynamics, the matrix solubility increasing was explained by the change of the gibbs free energy which was caused by plastic deformation, and the driving force for the dissolution was given. Finally, two dissolution models were proposed based on the orientation relationship between the copper precipitation and rolling surface.

2. Materials and experiments

2.1. Materials

Ideal antibacterial properties can be achieved only if copper content reaches above 1.3 wt% in Fe-17wt%Cr alloy, and the copper content should be reasonably higher to obtain desired antibacterial performance in practical testing [23]. But there is a serious problem in hot working due to surface hot shortness if the copper content is too high [24,25]. Some studies and the previous results of our group demonstrate that when 1.5% Cu was selected and annealed at proper temperature, enough copper precipitations can be obtained which can ensure excellent antibacterial performance [5,18,26,27]. The material in this study was received from Taiyuan Iron and Steel Corporation. The chemical composition of the material investigated is shown in Table 1. The material was forged and hot-rolled to a thickness of 4 mm. After a solution treatment of annealing at 970 °C for 5 min, the hot rolled sheets were cooled to room temperature in the air followed by antibacterial annealing. It has been demonstrated that only the volume fraction of copper precipitation is more than 0.5% the materials can get excellent antibacterial function [28]. And the volume fraction of copper precipitation as a function of temperature in Fe-17wt%Cr-1.5wt%Cu material, as shown in Fig. 1, was calculated by Thermo–Calc based on the thermodynamic database TCFE7. When the antibacterial annealing temperature is 800 °C, the volume fraction of copper precipitation approaches 0.6%. Some studies and the previous results of our group demonstrate that excellent antibacterial function can be obtained when annealed at 800 °C [18,26]. Therefore, the antibacterial annealing temperature was 800 °C in this paper. The plates were annealed at 800 °C for 6 h, and then cooled to room temperature. These slabs were cold rolled to 3.5, 3, 2, 1 mm thickness (12.5%, 25%, 50%, 75% in reduction), respectively. After antibacterial annealing the plates without cold rolling were marked as the undeformed sample.

Table 1
Composition analysis of experimental material (wt%).

C	Si	Mn	P	S	Cr	Ni	Cu	Fe
0.003	0.19	0.23	0.009	0.001	17.05	0.30	1.50	Balance

2.2. Microstructure characteristics

The morphology and microstructure evolutions of copper precipitations during cold rolling were observed by using scanning electron microscope (SEM, FEI Company, Hillsboro, USA) and transmission electron microscopy (TEM, FEI Tecnai F20). TEM samples were prepared by double-jet thinning in a reagent of 5% perchloric acid and 95% acetic glacial acid, and the voltage was 20 V and the temperature −20 °C. The micro-hardness was measured on a THV-1MD digital micro vickers hardness tester, with load of 500 g and loading time of 10 s. Before testing, the sample was grinded with 200-2000# sand papers and then polished.

2.3. X-ray diffractometry

The XRD samples were cut into plates with 20 mm × 25 mm in size, and the surfaces were milled on sand papers from 200# to 2000#. XRD tests were performed by using Cu–Kα radiation. And the scan rate and the scan step size were 1 deg. min^{-1} and 0.02 deg., respectively.

2.4. Antibacterial tests

The antibacterial rates were tested according to JIS Z 2801:2012 in Test Center of Antibacterial Materials, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences. The type of bacteria was *E. coli.* (ATCC 25922). Three antibacterial samples with size of 50 mm × 50 mm were ground to remove the rust layer and then sterilized by boiling at 121 °C for 20 min. The culturing solution containing the bacteria was diluted to $(2.5–10) \times 10^5$ cfu/mL. 0.4 mL of this solution was homogeneously added on the material, and then incubated at 35 ± 1 °C for 24 h. After incubation, the culturing solution containing the bacteria was separately diluted and added onto the nutrition agar plate and incubated at 35 ± 1 °C for another 24 h and the bacterial colonies