Study on the processing map of antibacterial Ti-10Cu sintered alloy

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Abstract. This paper studied the hot deformation behavior of Ti-10Cu sintered alloy in order to optimize the deformation processing. Ti-10Cu alloy was prepared by the powder metallurgy method to obtain strong antibacterial property. The deformation temperature range of 800°C to 1000°C and the strain rate range of 0.008 s⁻¹ to 5 s⁻¹ were chosen. The constitutive equation in hyperbolic sin function was established and the hot processing map was drawn based on the true stress-true strain curves. The microstructure and of the hot deformed alloy were observed in order to reveal the influence of the hot deformation on the microstructure. The results showed that the Ti₂Cu phase distributed homogeneously with increasing in the deformation temperature and decreased with the increasing of the strain rate. The final optimized deformation process was: a deformation temperature range of 850°C to 950°C, and a strain rate of 0.1s⁻¹ to 0.5s⁻¹, where a completely homogeneously distributed microstructure would be obtained.

1. Introduction

It was reported that surgical site infection represents the most common nosocomial infection, accounting for 15% of all nosocomial infections[1]. Pastides P. found periprosthetic infections in orthopaedics occur with a high frequency in primary hip and knee arthroplasties[2]. The main reasons are the colonization of bacteria on the materials surfaces and the formation of biofilm, showing a 500-5000 times more resistant to antimicrobials as compared to planktonic bacteria[3]. In our previous studies, the Ti-10wt.%Cu alloy prepared by a powder metallurgy showed very strong antibacterial property against Staphylococcus aureus and Escherichia Coli, and good biocompatibility and corrosion resistance[4]. Despite of those advantages, the brittleness of the sintered Ti-10wt.%Cu alloy limits its uses. Hot extrusion is an effective method to improve the ductility of sintered titanium alloy by homogenizing the microstructure and eliminating the microstructure defects[5]. A new β metastable titanium alloy Ti-20.6Nb-13.6Zr-0.5 alloy had better mechanical biocompatibility after a set of thermo-mechanical processing[6]. Thus, whether the Ti-10Cu sintered alloy shows good antibacterial property after hot deformation has high research value.

2. Methods

2.1. The method of preparative titanium-10wt.%copper sintered alloy

High purity Ti powder and Cu powder were mixed for 24h with a nominal composition of Ti-10wt.%Cu in a ball mill. The mixed powder was cold pressed by 300MPa, high pressure and vacuum
sintered at 1000°C for 3h under 35MPa in a graphite mould and cold down to room temperature in furnace to obtain a cylindrical Ti-10Cu ingot with 40 mm in diameter and 30 mm in height. Samples for the compression test with a dimension of 8 mm in diameter and 12 mm in height were sliced from the sintered ingot by wire-electrode cutting method.

2.2. Isothermal compressive test
All samples before test were ground by SiC papers up to 2000 grits and polished by 1µm polishing paste. The isothermal compressive test was conducted on a MMS-200 machine thermal simulator at temperatures of 800°C, 850°C, 900°C, 950°C and 1000°C with a temperature control accuracy of ±5°C, maximum true strain of 0.6, and strain rates of 0.004s⁻¹, 0.02s⁻¹, 0.1s⁻¹, 0.5s⁻¹ and 1s⁻¹.

2.3. Representation of microstructure
Before and after compression, the specimens were sectioned along the longitudinal section for microscopic examination. The metallographic sample was ground and polished as described above and then etched in a mixture of 5% HF+15% HNO₃+ 80% alcohol. The metallographic structure was observed by optical microscope and scanning electron microscope.

3. Results

3.1. Constitutive equations of Ti-10wt.%Cu alloy
The deformation temperature T(°C) and the strain rate \( \dot{\varepsilon} (s^{-1}) \) influence the flow stress during the hot deformation process. The relationship between the flow stress (\( \sigma \)), the strain rate (\( \dot{\varepsilon} \)) and the deformation temperature (T) of a metal during a hot deformation process is generally described by a hyperbolic sine function equation given by Budrugeac P [7]. Based on this equation, the constitutive equation of Ti-10wt.%Cu hot deformation is established as following:

\[
\dot{\varepsilon} = A_1\sigma^n\exp\left(-\frac{Q}{RT}\right) \tag{1}
\]

\[
\dot{\varepsilon} = A_2[\exp(\beta\sigma)]\exp\left(-\frac{Q}{RT}\right) \tag{2}
\]

\[
\dot{\varepsilon} = A[\sinh(\alpha\sigma)]^n\exp\left(-\frac{Q}{RT}\right) \tag{3}
\]

where \( A_1, A_2, A, n_1, n, \alpha \) and \( \beta \) are the material constants which have no relation with temperature, \( \alpha, \beta \) and \( n_1 \) have a relation that \( \alpha = \beta/n_1 \), \( \dot{\varepsilon} \) is the strain rate (1/s), \( \sigma \) is the flow stress (MPa), R is the universal gas constant (8.3145J mol⁻¹K⁻¹), T is the absolute deformation temperature(K), and Q is the activation energy for the hot deformation (KJ/mol).

Strain 0.6 is taken for an example, and by taking natural logarithm for both sides of Eq. (1) Eq.(2)and Eq.(3), it can be expressed by:

\[
\ln \dot{\varepsilon} = \ln A_1 + n_1\ln \sigma - \frac{Q}{RT} \tag{4}
\]

\[
\ln \dot{\varepsilon} = \ln A_2 + \beta\sigma - \frac{Q}{RT} \tag{5}
\]

\[
\ln \dot{\varepsilon} + \frac{Q}{RT} = \ln A + n\ln[\sinh(\alpha\sigma)] \tag{6}
\]

Figure 1 shows the experimental flow stress curves (lines) at different deformation temperatures and different strain rates. From Eq.(6), it can be found that when the strain rate (\( \dot{\varepsilon} \)) is constant, the natural logarithm of strain rate (\( \ln \dot{\varepsilon} \)) and natural logarithm of nominal peak stress in Figure 1(\( \ln[\sinh(\alpha\sigma)] \)) shows a linear relationship. Meanwhile, when the strain rate (\( \dot{\varepsilon} \)) is constant, the natural logarithm of nominal peak stress (\( \ln[\sinh(\alpha\sigma)] \)) and the reciprocal of absolute temperature (1/T) also show a linear relationship.
Figure 1. Experimental flow stress curves (lines) and the simulated (line+symbol) flow stress at temperatures (a) 800°C; (b) 850°C; (c) 900°C; (d) 950°C; (e) 1000°C.

The values of $n_1$ and $\beta$ can be obtained from the slopes of the linear fittings of $\dot{\varepsilon} - \ln \sigma$ plots and $\dot{\varepsilon} - \sigma$ plots, as shown in Figure 1a and Figure 1b, respectively, when the temperature is certain. After taking average, the value of $n_1$ and $\beta$ were obtained as $n_1=3.278$ and $\beta=0.0789$, so $\alpha=0.0241$.

From the slopes of the linear fittings of $\dot{\varepsilon} - \ln(\sinh(\alpha \sigma))$ plots, shown in Figure 1c, the value of $n$ can be obtained. After taking average, the value of $n$ was obtained as $n=2.3138$. From Figure 1d, the hyperbolic sine logarithm of $\sigma$ and the reciprocal of the temperature have roughly a linear relation at same strain rate. Therefore, the hot compression flow stress ($\sigma$) of Ti-10Cu alloy and the deformation temperature meet the Arrhenius relation, and the hot deformation of Ti-10Cu alloy was controlled by an activation process.

After taking partial differential of both sides of Eq. (6), the following equation was obtained:

$$Q = R \left( \frac{\partial \ln \dot{\varepsilon}}{\partial \ln(\sinh(\alpha \sigma))} \right) \left( \frac{\partial \ln(\sinh(\alpha \sigma))}{\partial (\frac{1}{T})} \right).$$

(7)
The value of $Q$ was obtained to be 461.005 kJ/mol.

From Eq. (7) and Figure 1c, the intercept of the $\ln \varepsilon - \ln [\sinh (\alpha \sigma)]$ fitting linear is the value of $\ln A - Q/RT$. After taking average of the values of $\ln A$ at different temperatures from the values of $Q$, $R$ and $T$, then $\ln A = 17.47$. Thus, the value of material constant $A$ is $5.07 \times 10^{14}$. The values of parameters $\alpha$, $n$, $A$, $Q$ at other strains were obtained according to the above process, as listed in Table 1. From Eq.(3), the constitutive equation was obtained:

$$\sigma = \left(\frac{1}{\alpha}\right) \ln\left(\frac{Z}{A}\right)^{1/n} + \left(\frac{Z}{A} \right)^{2/n} + 1)^{1/2}$$

(8)

where,

$$Z = \varepsilon \exp\left(\frac{Q}{RT}\times 10^3\right)$$

(9)

Table 1. Polynomial parameter $\alpha$, $n$, $A$, $Q$ at different strains of Ti-10Cu alloy.

| $\varepsilon$ | $\alpha$   | $n$     | $A$           | $Q$           |
|-------------|-----------|--------|---------------|---------------|
| 0.1         | 0.022650  | 2.497760 | 1.10E+11      | 400.4847      |
| 0.2         | 0.022807  | 2.445700 | 1.05E+10      | 368.4107      |
| 0.3         | 0.023064  | 2.403052 | 1.17E+09      | 337.7484      |
| 0.4         | 0.023509  | 2.357152 | 2.42E+08      | 317.0291      |
| 0.5         | 0.023811  | 1.148300 | 1.13E+08      | 149.1342      |
| 0.6         | 0.024069  | 2.313868 | 3.87e+07      | 292.4900      |

Figure 2 also shows the predicted flow stress curves (line + symbol in same color) at different deformation temperatures and different strain rates. The result shows that the predicted values roughly fit the experimental flow stress, especially at the high strain range.

(a) [Graph representation] (b) [Graph representation] (c) [Graph representation] (d) [Graph representation]

Figure 2. Relationship during hot compression of Ti-10Cu alloy.

(a) $\ln \dot{\varepsilon} - \dot{\sigma}$ (b) $\ln \dot{\varepsilon} - \dot{\sigma}$ (c) $\ln \dot{\varepsilon} - \ln [\sinh (a\sigma)]$ (d) $\ln [\sinh (a\sigma)] - (1/T)$. 


3.2. Processing maps for Ti-10wt.%Cu biomedical alloy

Processing map is based on the principles of the dynamic material model, which not only describes the deformation mechanism of a specific microstructure, but also describes the flow instability domains need to avoid during thermal processing [8]. Therefore, the processing map is helpful to the formulation and optimization of the hot processing parameter in actual production.

The efficiency of power dissipation (η) is defined physically as the ratio of the power dissipater of the microstructure evolution to the linear dissipation during the hot deformation, the parameter, η can be given by [9]:

\[
\eta = \frac{J}{J_{\text{max}}} = \frac{2m}{m + 1}
\]  

(10)

where, m is a strain rate sensitivity parameter of flow stress.

A continuum instability criterion based on the extremum principles of irreversible thermodynamics as applied to large plastic flow is used in this study to identify the flow stability regions. The principle of maximum rate of entropy production in metallurgical system results in an instability criterion was described as the following expression [10]:

\[
\varepsilon' = \frac{\partial \ln \frac{m}{m + 1}}{\partial \varepsilon} + m < 0
\]  

(11)

The processing map is the superimposition of a power dissipation map and an instability map, which represent the “safe” domain and “unsafe” domain during plastic processing, respectively. The negative value region in the two dimensional coordinate system of the strain rate and temperature is namely the instability region of hot work. According to the processing map, in the stability region, the bigger η value is, and the better the workability of the alloy is. Thus, the optimum hot work technology parameter can be determined.

The processing maps of Ti-10wt.%Cu sintered alloys at different strains were shown in Figure 3. It can be seen that the efficiency of power dissipation (η) was high at high temperature (>950°C) and high strain rate (>0.5s^{-1}) as well as at the low temperature (<850°C) and low strain rate (<0.1s^{-1}). Meanwhile, all the instability regions occurred at low temperature and high strain rate, indicating the rate of crystallization was much less than the rate of deformation. Above all, the deformation temperature of 900°C and the strain rate of lower than 0.1s^{-1} were the desired working region with the efficiency of power dissipation of 45-50%.

![Figure 3. Power dissipation and instability diagrams of Ti-10Cu alloy (a) ε=0.2, (b) ε=0.4, (c) ε=0.6(The tinctorial parts represent the instability domains).](image)

3.3. Microstructure

Figure 4 shows the photos of Ti-10Cu samples deformed at different temperatures and strain rates. Obvious cracks were found on the samples deformed at low temperature and high strain rate, such as at 800°C/1s^{-1}, 800°C/0.5s^{-1} and 850°C/1s^{-1}, but no crack was found on the samples deformed at other...
processing parameters, corresponding to the processing map where the instability region occurred at low temperature (<850°C) and high strain rate (>0.5s⁻¹).

Figure 4. Photos of Ti-10wt.%Cu samples deformed at different temperatures and strain rates.

Figure 5a shows the undeformed microstructure of sintered Ti-10Cu alloy. Figure 5b~f show the microstructure of Ti-10Cu alloys deformed at different temperatures with a strain of 0.6 and strain rate of 0.004s⁻¹. Typical Ti₂Cu phase (lamellar-type) and Cu-rich phase (block-type) distributed discontinuously in the matrix (as shown in Figure 5a) which were systemically studied in our previous research[5]. After deformation, the grain was elongated along the vertical deformation direction and the size of secondary phase (Ti₂Cu phase and Cu-rich phase) were decreased. Even when the deformation temperature exceeded 950°C, the secondary phase showed fine size and distributed homogeneously in the matrix.

Figure 5. The vertical microstructure of the deformed Ti-10Cu alloy at a strain rate of 0.004s⁻¹ and different temperatures (ε= 0.6) (a) undeformed alloy; (b) 800°C; (c) 850°C; (d) 900°C; (e) 950°C; (f) 1000°C.

4. Conclusions
The hot deformation behavior and the processing maps for antibacterial Ti-10Cu sintered alloy have been studied at a temperature range of 800°C~1000°C with a strain rate of 0.004~1s⁻¹. The following conclusions can be drawn from the investigation:
(1) The apparent activation energy of deformation was obtained to be 364483 J/mol. The hot deformation equation of Ti-10wt.%Cu alloy can be expressed as:

\[
\varepsilon = 5.07 \times 10^{14} \left[ \sinh \left( \frac{0.021\varepsilon}{\sigma} \right) \right]^{2.06} \exp \left( -364.4 \frac{83}{RT} \right)
\]

(2) The instability region occurred at higher strain rates (>0.5s\(^{-1}\)) and lower temperatures(<850°C), which should be avoided during hot deformation for the powder metallurgy Ti-10Cu alloy. The optimal working region obtained from the processing map appears at 900°C and the strain rate of lower than 0.1s\(^{-1}\) with the efficiency of power dissipation of 45-50%.

(3) Ti-10Cu alloy obtain homogenized microstructure after hot deformation.

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