



Rapid communication

Creep behavior of two Cu-2 vol% TiC alloys obtained by reaction milling and extrusion



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ABSTRACT

The creep behavior of two Cu-2 vol% TiC alloys prepared by reaction milling and extrusion are presented. Creep tests were performed at 773–1123 K. The activation energy values between 109 and 156 kJ/mol and the stress-exponent values between 3.1 and 6.3 indicated that no dispersion-strengthening effect occurred.

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1. Introduction

Alloys exhibiting high mechanical strength combined with high electrical and thermal conductivity at elevated temperatures are in increasing demand [1]. Because it has high electrical/thermal conductivity, copper is a promising metal for these types of applications if its high-temperature strength could be improved.

On the other hand, the creep properties of pure metals are often characterized through the dependence of secondary creep rate $\dot{\epsilon}$ on stress (σ) and temperature (T) using power law equations as follows [2]:

$$\dot{\epsilon} = A\sigma^n \exp\left(\frac{-Q}{RT}\right) \quad (1)$$

where R is the gas constant. The parameter (A), the stress exponent (n), and the activation energy for creep (Q) are also functions of stress and temperature. Also, for a given T value the above expression may be written as

$$\dot{\epsilon} = B\sigma^n \quad (2)$$

As reviewed by Langdon [3], over a wide range of high and intermediate stresses, the steady-state creep rate in pure metals and their solid solutions varies with stress raised to a reasonable high power of n (~ 3 – 5). In this region the flow is dominated by the intragranular movement of dislocations: this behavior is generally termed power-law creep. At even higher stresses, the

creep rate varies exponentially with stress where this behavior marks a transition from diffusion-controlled flow at the lower stresses to a thermally-activated region analogous to flow at low temperatures. This transition is generally termed the power law breakdown (PLB). The flow mechanism is also characterized by the activation energy Q in relation to the controlling diffusive process. On the other hand, dispersion-strengthened materials, in comparison with pure metals and solid solutions, present higher n and Q apparent values [4].

The high-temperature strength of metallic alloys may be increased by adding a small fraction (e.g., between 2 and 5 vol%) of ceramic dispersoids. Several researchers have demonstrated that the addition of appropriate nanometric dispersoids may increase the creep resistance of copper based alloys [4–6]. Adding elements that form insoluble particles affects the electrical conductivity less than forming a solid solution. These dispersoids must be thermodynamically stable, nanometric in size, and homogeneously distributed within the metal matrix [1]. Additionally, when ceramic dispersoids are present, the strength of the material at high temperatures is primarily controlled by dislocation-particle [7] and grain boundary-particle interaction [8]. Reaction milling is a modern process that uses mechanical alloying to the in-situ development of nanometric dispersoids within a metal matrix [9]. Elemental powders are milled under a specific atmosphere combined with a liquid milling media to allow one or more metals to react with C, N, or O. Microcrystalline grains develop a high dislocation density because of attrition. This process also requires that the milled powders be consolidated using thermomechanical approaches, such as hot extrusion. In our previous studies [10,11], different dispersion-strengthened Cu alloys were prepared by

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reaction milling, in a small high-energy ball mill (Spex 8000D) and a medium-energy home-made attritor mill.

The aim of the present work is the study of the creep behavior of two Cu-2 vol% TiC alloys prepared by reaction milling in an attritor or Spex mill followed by hot extrusion. The effects of creep temperature, strain rate, and milling procedure were examined.

2. Experimental procedure

Two nominally composed Cu-2 vol% TiC alloys were produced by reaction milling from dendritic elemental powders of Cu (85 wt% under 40 μm) and Ti (< 45 μm). The milling process was performed in a Szegvari-type attritor or Spex mill, with rotational speeds of 500 rpm or 1.200 rpm, and milling times of 30 h or 10 h, respectively. All millings utilized a ball to powder weight ratio of 10:1, a nitrogen atmosphere, and toluene as the milling medium. The C necessary to form the nanodispersoids in-situ was provided by toluene. The resulting aggregates were encapsulated under low vacuum before being consolidated using hot extrusion at 1023 K and with a 10:1 extrusion ratio. These experimental conditions were based on previous results in our laboratory. Compression-test cylindrical specimens 6 mm in diameter and 10 mm in length were machined from the as-extruded bars such that the machined axis was parallel to the extrusion direction. Constant-stress compression creep tests were performed in a TT-DM Instron machine equipped with a high-temperature compression device, at 773,

973 and 1123 K; the utilized loads produced steady-state creep rates between 1.1×10^{-9} and $2 \times 10^{-6} \text{ s}^{-1}$. X-ray diffraction (XDR) was performed with a Siemens D5000 system. The density was determined using the Archimedes method.

3. Results and discussion

The chemical analyses of the powders treated in the Spex and in the attritor mills are presented in Table 1. With the Ti content and the excess C detected, vol% TiC values were calculated for each alloy, as indicated in Table 1; the vol% TiC values calculated for the Spex- and attritor- treated alloys, were 2.1 and 2.2, respectively. Additionally, O and Fe contamination was also detected; the former most likely originated from the N_2 gas and surface Cu oxides, while the latter arose from the steel milling balls. The measured density of both extruded alloys was approximately 95% of the theoretical density.

In Fig. 1, XRD diagrams of the Cu-Ti powders formed under different processing conditions are shown. Fig. 1(a) depicts the expected XRD data for powders immediately after blending; only peaks associated with Cu were detected. However, in Fig. 1(b) and (c), corresponding to the powders milled in the Spex and attritor facilities, respectively, a small maximum at a diffraction angle $2\theta = 41.9^\circ$ appears in addition to the Cu peaks. A peak at this angle might be ascribed to the most intense TiC reflection at the {200}

Table 1
Chemical composition of Cu-Ti-C powders.

Element	Calculated element amounts in wt%, to obtain a Cu-2 vol%TiC alloy	Measured amounts, wt%	
		Spex milled powders	Attritor milled powders
Ti	2.25 ^a	0.93	1.03
C	0.56 ^a	1.21	0.69
O	–	0.37	0.59
Fe	–	0.10	0.17
TiC vol%		2.1 ^b	2.2 ^b

^a Assuming a 50 wt% loss of each element, similar to previous results.

^b Calculated for the measured Ti wt% with C in excess.

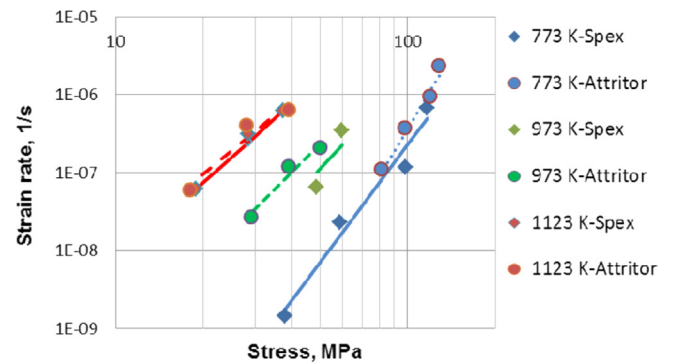


Fig. 2. Effects of compression stress on the strain rate at different temperatures for the alloys.

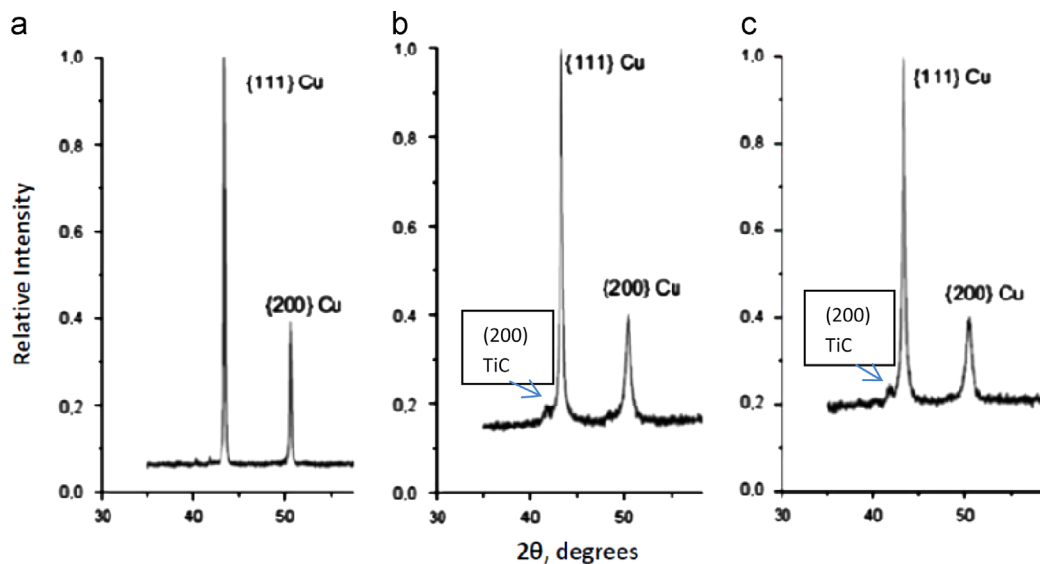


Fig. 1. XRD diagrams of Ti-C powders under different processing conditions: (a) immediately after blending; (b) after milling in the Spex facility; and (c) after milling in the attritor facility.

Table 2

Values for the n exponent and B constant determined for the Cu–Ti–C alloys at different temperatures.

Temperature, K	Spex milled and sintered powders		Attritor milled and sintered powders	
	n	B , MPa ^{-n} s ⁻¹	n	B , MPa ^{-n} s ⁻¹
773	4.8	1.9×10^{-17}	6.3	8.6×10^{-20}
973	4.0	1.8×10^{-14}	3.8	8.2×10^{-14}
1123	3.4	2.8×10^{-12}	3.1	9.0×10^{-12}

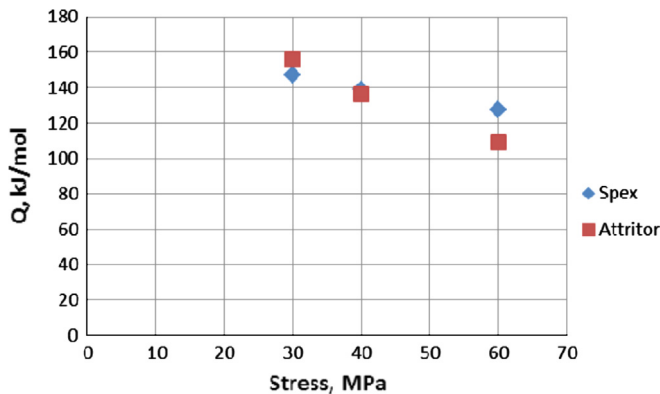


Fig. 3. Activation energy as a function of stress for specimens produced in a Spex or attritor mill.

plane [12]. Therefore, TiC particles were formed during both of the milling procedures.

The results of the creep tests performed at different temperatures and stresses verified Eq. (2); the experimental data exhibits a reasonable linear fit in a $\log \sigma$ versus $\dot{\epsilon}$ plot for different temperatures, see Fig. 2. Only two experimental points were available for the alloy processed in the Spex mill at 973 K and were used in place of the three intended points; the n value (Eq. (2)) for that equipment and temperature was calculated by interpolating the n values obtained using the other two temperatures (773 and 1123 K) on the same equipment. Afterwards, using the calculated n value a straight line was determined via least squares regression and the fit for the two experimental points is available in the \log – \log plot in Fig. 2.

The results in Fig. 2 indicate that, as expected, the creep resistance decreased ($\dot{\epsilon}$ increased) when temperature increased. For a given creep temperature, no significant difference was detected between the alloys prepared in the Spex (10 h milling time) or the attritor (30 h milling time) mills. The creep exponent n values obtained as the slope of the straight lines presented in Fig. 2, were between 3.1 and 6.3, as displayed in Table 2. These n values were significantly smaller than expected (20–100) for alloys with observed dispersion strengthening [11–13]; the present n values correspond to the values for pure metals or metallic solid solutions [14].

On the other hand, the following expression can be derived from Eq. (1) to calculate Q :

$$Q = -R \left(\frac{\partial \ln \dot{\epsilon}}{\partial (1/T)} \right)_{\sigma} \quad (3)$$

Subsequently, the strain rate was calculated for different stresses by employing the n and B values from Table 2, for each straight line in Fig. 1. For each stress value, a linear relationship between $\ln \dot{\epsilon}$ and $1/T$ was found (with a correlation coefficient $R^2 > 0.99$); therefore, Q is temperature independent within the

studied temperature range. The Q values obtained using Eq. (3) at different stresses for the two alloys are displayed in Fig. 3. The two materials exhibited similar behavior: the pertinent (Q , σ) points were next and Q decreased as σ increased.

The σ range presently covered (30–60 MPa) corresponded to a σ/G range between 0.77×10^{-3} and 1.54×10^{-3} , where G is the Cu shear modulus; the dependence of G with T was here considered [15] for the necessary σ/G calculation. The said σ/G range lies within the range observed by Raj and Langdon [16] as being associated to the PLB transition in Cu, where non-diffusion controlled mechanisms are dominant and are likely to be stress dependent. Also, our Q values were reasonably near to those previously informed [16] for Cu within the specified σ/G range. It is then inferred that our results might correspond to creep in the PLB region.

Consequently, our n and Q values were much lower than the values usually attributed to creep in dispersion-strengthened copper alloys [4,5–11]. Notably, the presence of nanometric (7 nm) TiC particles was verified using TEM in the Spex milled alloy [17]. Therefore, even though the formation of TiC was detected by XRD in both alloys, the studied materials did not exhibit a significant dispersion hardening effect.

4. Conclusions

It is concluded that the creep behavior of the two nominally composed Cu-2 vol% TiC alloys prepared by reaction milling in a Spex or attritor facility is as follows:

1. During milling, TiC is formed in both alloys, as detected by XRD.
2. The creep resistances obtained for the consolidated powders are similar in both alloys.
3. The n and Q values obtained during the creep tests, which are similar in both alloys, suggest that no dispersion-hardening occurred.

Novelty

The author formally states that the manuscript “Creep behavior of two Cu-2 vol% TiC alloys obtained by reaction milling and extrusion”, authored by Rodrigo H. Palma and Aquiles O. Sepúlveda, submitted for publication to the Journal of Materials Science A under the code MSEA-D-12-04083R1, is an original work developed at my laboratory, Dept. Mech. Eng., Universidad de Chile, Santiago, Chile.

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