Research Article

Thermal Conductivity of Cu-Cr-Zr-Ti Alloy in the Temperature Range of 300–873 K

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In the present investigation, thermal conductivity of Cu-Cr-Zr-Ti alloy was determined as the product of the specific heat (C_p), thermal diffusivity (α), and density (ρ) in the temperature range of 300–873 K. The experimental results showed that the thermal conductivity of the alloy increased with increase in temperature up to 873 K and the data was accurately modeled by a linear equation. For comparison, thermal conductivity was also evaluated for OFHC copper in the same temperature range. The results obtained were discussed using electrical conductivity and hardness measurements made at room temperature. Transmission electron microscopy (TEM) was done to understand the microstructural changes occurring in the sample after the test. Wiedemann-Franz-Lorenz law was employed for calculating electronic and phonon thermal conductivity using electrical conductivity. On the basis of studies conducted it was deduced that in situ aging may be one of the reasons for the increase in thermal conductivity with temperature for Cu-Cr-Zr-Ti alloy.

1. Introduction

Cu-Cr-Zr alloy is a candidate material for high heat flux applications like the inner wall of a thrust chamber and the first wall of nuclear reactor owing to its high conductivity and strength [1, 2]. The high conductivity of the alloy is attributed to the low solubility of Cr and Zr in copper at room temperature [3], while the strength is due to the precipitation of Cr and Cu_5Zr in copper matrix [4, 5]. Zirconium plays an additional role of fixing elemental sulphur and suppresses dynamic embrittlement [6]. The alloy used in the present study is modified by the addition of titanium of Cu-Cr-Zr alloy. Titanium plays a role similar to that of zirconium in Cu-Cr-Zr alloy in suppressing dynamic embrittlement by fixing elemental sulphur as titanium sulphide [7]. Limited literature is available on mechanical properties, microstructure and thermal properties of Cu-Cr-Zr-Ti alloy. Lack of thermal conductivity data for the alloy at

elevated temperature promoted us to design experiments to evaluate the same in the temperature of 300–873 K.

2. Experimental Procedure

Hot rolled and annealed plate of Cu-0.61Cr-0.038Zr-0.029Ti-0.003Fe (wt %) alloy was used in the present study. Small pieces cut from the plate were used for hardness, thermal, and electrical conductivity measurement. In addition, properties of OFHC copper (C10100) were evaluated in the annealed condition. OFHC copper represents the pure form of copper, and the effect of alloying elements (Cu-Cr-Zr-Ti) can be better understood by comparison. Thermal conductivity was measured using a Flashline 3000 laser flash apparatus as the product of thermal diffusivity (α), specific heat (C_p), and density (ρ). A disc of 12.7 mm diameter and 3 mm thickness was used for the measurement. The samples were made more opaque to the energy pulse by coating with

FIGURE 1: Effect of temperature on the thermal conductivity of OFHC copper and Cu-Cr-Zr-Ti alloy.

a thin layer of graphite spray. Three tests were conducted in the temperature range of 300–873 K, and average of three tests is reported. Hardness of the disc was measured at room temperature before and after thermal conductivity test using the Brinell Hardness Tester. An average of five hardness readings is reported. The electrical resistivity was determined using four-point technique by measuring the resistance of the specimens (50 mm (length) $\times$ 4 mm (width) $\times$ 6 mm (thickness)) utilizing meter calibrator-Wavetek 9100 and digital multimeter-HP 3458. Thin foils for TEM were prepared by mechanical polishing, dimpling, and ion milling. Discs of 3 mm diameter and 100 μ m thick were punched, and one side was dimpled followed by ion milling with an incident beam angle of 4° using Gatan PIPS system. The ionmilled thin foils were examined under a JEOL transmission electron microscope operated at 200 kV.

3. Results and Discussion

Thermal conductivity of OFHC copper and Cu-Cr-Zr-Ti alloy as a function of temperature is shown in the Figure 1. OFHC copper shows a decreasing trend with an increase in temperature, and λ decreases from 397 Wm⁻¹K⁻¹ at 300 K to 350 Wm⁻¹K⁻¹ at 873 K. The observed trend is in agreement with previous works [8–11]. On the other hand, λ of Cu-Cr-Zr-Ti alloy increases with increase in temperature up to 873 K. The room temperature thermal conductivity was measured as 279 Wm⁻¹K⁻¹, while it reaches 337 Wm⁻¹K⁻¹ at 873 K. The data obtained for OFHC copper and Cu-Cr-Zr-Ti alloy could be correlated to a second degree polynomial and linear equation, respectively, as shown in Table 1.

It was also found that the thermal conductivity of Cu-Cr-Zr-Ti alloy is lower than OFHC copper in the temperature range investigated. However, the gap between the curves was more at room temperature, and it diminished with increase in temperature. A similar increasing trend of thermal

conductivity with temperature was reported in copper alloys [9, 10], platinum alloys [12], tungsten alloys [13], and magnesium alloys [14, 15]. The reason for lower thermal conductivity for alloys can be attributed to the alloying elements added to the matrix. These elements impede the movement of free electrons, which are the primary source for heat transport in metals and alloys by acting as scattering sites and decreasing the mean free path [11]. Nevertheless, the magnitude of drop in thermal conductivity depends on the position of an element in the periodic table and the concentration of the element [12, 16].

The thermal conductivity of the metals and alloys is assumed to compose of an electronic component (λ_e) and a phonon component (λ_p) [13]:

$$\lambda = \lambda_e + \lambda_p. \quad (1)$$

The electronic thermal conductivity can be approximately calculated using Wiedemann-Franz-Lorenz Law:

$$\lambda_e = L\sigma T, \quad (2)$$

where L is the Lorentz number (2.443×10^{-8} W Ω K⁻²), σ is the electrical conductivity (Ω m)⁻¹, and T is temperature (K)

$$\begin{aligned} \lambda_e(\text{Cu-Cr-Zr-Ti}) &= (2.443 \times 10^{-8}) \cdot (0.3386 \times 10^8) \cdot 300 \\ &= 248 \text{ Wm}^{-1}\text{K}^{-1}. \end{aligned} \quad (3)$$

λ_p (Cu-Cr-Zr-Ti) is calculated as 31 Wm⁻¹K⁻¹ ($\lambda - \lambda_e$: 279 – 248). This indicates that the electron contribution is dominant for the alloy at room temperature.

It is noteworthy to mention that the addition of impurities largely reduces the electronic thermal conductivity (λ_e) of the alloy. This can be substantiated by comparison of λ_e for OFHC copper and Cu-Cr-Zr-Ti alloy at room temperature. The λ_e obtained for OFHC copper and Cu-Cr-Zr-Ti alloy was 398 Wm⁻¹K⁻¹ and 248 Wm⁻¹K⁻¹, respectively, which clearly shows that λ_e for the alloy is suppressed due to alloying elements. This result is in line with that obtained for MgSc alloys, where it was reported that significant change has been noticed in λ_e with the concentration of the alloying element added to the alloy [14, 15].

It is seen from the Figure 1 that the thermal conductivity of Cu-Cr-Zr-Ti alloy increases with temperature up to 873 K. The reason for such increasing trend to a larger extent may be attributed to the increase in electronic thermal conductivity with temperature [13–15]. Nevertheless, some contribution can be ascribed to microstructural changes occurring in the specimen during the test. The alloy studied can attain age hardening in the temperature range of 673–823 K [3, 4]. In the present study, tests were conducted in the temperature range of 300–873 K and at each test temperature, and the sample was held for 30 min for attaining homogeneity. Therefore, there is a reason to believe that in situ aging might have occurred, which has contributed to the increase in thermal conductivity with temperature. This argument was supported by measuring the hardness of the disc after the

TABLE 1: Results of regression analysis for α , C_p , and λ and temperature for OFHC copper and Cu-Cr-Zr-Ti alloy.

Property	Material	Equation	Regression constant (R^2)	Valid range
Thermal conductivity (λ)	OFHC Cu	$\lambda = 461.1 - 0.22(T) + 1.20 \times 10^{-4}(T^2)$	0.9490	300–873 K
	Cu-Cr-Zr-Ti	$\lambda = 253.5 + 0.099(T)$	0.9123	300–873 K

FIGURE 2: Transmission electron microscopy images of thermal conductivity specimens (a) before test, (b) after test, (c) EDS spectrum from (a), and (d) selected area diffraction from (b).

test. The hardness of the disc before the thermal conductivity test was 70 BHN, and after the test, it has increased to 91 BHN, which shows that hardening has occurred in the sample. The possible mechanism which enables hardening in the given temperature range of the alloy is in situ aging. In situ aging will result in the precipitation of excess element,

which will make the matrix pure (rich in Cu), and increases the thermal conductivity.

The transmission electron microscopy images of the thermal conductivity specimens before and after the test are shown in Figure 2. The bright-field image of the specimen before the test is shown in Figure 2(a) with modulated

structure free of any precipitates. Figure 2(b) shows the bright-field image of the specimen after the test where a uniform distribution of fine precipitates is observed in the matrix. The energy dispersive X-ray spectroscopy (EDS) analysis spectrum obtained from the sample before the test (Figure 2(a)) is shown in Figure 2(c). The spectrum shows prominent peaks of copper with few peaks of chromium. From the spectrum, it can be inferred that the sample is in the solution treated condition with excess chromium in the copper matrix. The selected area diffraction (SAD) pattern taken from Figure 2(b) is shown in Figure 2(d). The spot pattern obtained was solved and indexed for matrix and precipitate. The matrix had FCC crystal structure corresponding to copper, and precipitate has BCC crystal structure corresponding to chromium. The matrix and precipitate are indicated with subscripts Cu and Cr, respectively. From TEM studies, it is inferred that precipitates that form in the specimen after the test is chromium precipitates, and similar Cr precipitates were reported by Batra et al. [3, 4]. In addition to hardness measurement, TEM studies clearly confirm the occurrence of in situ aging in the specimen after the test.

4. Conclusions

The investigation of thermal conductivity of Cu-Cr-Zr-Ti alloy in the temperature range of 300 K–873 K showed that the thermal conductivity is sensitive to temperature. With an increase in temperature, thermal conductivity showed an increase up to 873 K. Thermal conductivity increased by 20 % at 873 K compared to that at room temperature. In addition to electronic thermal conductivity, one of the reasons for the increasing trend with temperature is in-situ aging of the sample which results in formation of precipitates and facilitates precipitation of excess solute from the matrix. The curve obtained for thermal conductivity could be modeled to a linear equation. Electronic and phonon thermal conductivity of the alloy was calculated using Wiedemann-Franz-Lorenz law, and it was found that the phonon contribution was insignificant at room temperature.

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