INFLUENCE OF PHASE TRANSITIONS IN AuCu ON THERMAL DIFFUSIVITY AND THERMAL CONDUCTIVITY

ALEXANDRA RUDAJEVOVÁ[1]

Measured thermal diffusivity of AuCu alloy at temperatures 20–550 °C is presented and analysed. Thermal conductivity of ordered and disordered AuCu alloy was calculated as a product of the thermal diffusivity, specific heat and density. By using Wiedemann-Franz law and literature data for electrical resistivity, electronic and phonon thermal conductivities were calculated for ordered and disordered phases. While the phonon thermal conductivity is nearly the same for the ordered and disordered AuCu alloy, the electronic thermal conductivity of the ordered alloy is almost three times larger than that of the disordered one.

K e y w o r d s: intermetallic alloys, phase transitions, thermal diffusivity, thermal conductivity

VLIV FÁZOVÝCH PŘECHODŮ VE SLITINĚ AuCu NA TEPLOTNÍ A TEPELNOU VODIVOST

Teplotní vodivost slitiny AuCu byla měřena v teplotní oblasti 20–550 °C. Tepelná vodivost, která byla získána jako součin teplotní vodivosti, měrného tepla a hustoty, byla při pokojové teplotě dvakrát větší pro slitinu v uspořádaném stavu než pro slitinu v neuspořádaném stavu. Užitím Wiedemannova-Franzova zákona a literárních dat elektrického odporu byla stanovena elektronová a fononová tepelná vodivost pro uspořádaný a neuspořádaný stav slitiny. Zatímco fononová tepelná vodivost je téměř stejná pro uspořádaný a neuspořádaný stav, elektronová tepelná vodivost uspořádané slitiny je téměř třikrát větší než neuspořádané slitiny.

1. Introduction

Ordered intermetallic alloys have long been of interest as potential structural materials for use at elevated temperatures. Much attention has been paid to their mechanical, chemical and thermodynamic properties [1]. Thermal conductivities of

[1] Department of Metal Physics, Charles University, Ke Karlovu 5, 121 16 Praha 2, Czech Republic

intermetallic compounds have not been well characterized yet, though the knowledge of the thermal conductivity is necessary for high temperature applications. It is important for these materials to have a high thermal conductivity to push the operating temperature of structural materials to higher values because of their cooling ability. Also, the high thermal conductivity assures uniform temperature distribution, which reduces thermally-induced stresses and, thereby, improves fatigue properties. When cooling from melt or from thermal annealing, most intermetallic materials undergo disorder-order phase transformations. Therefore, it is important to know the difference between the thermal conductivities of single phases. Temperature dependence of the thermal conductivity of intermetallic materials is almost absent in literature.

The thermal conductivity of A_3B intermetallic compounds was investigated as a function of composition from the viewpoint of the periodic table [2]. For B2 and $L1_2$ compounds, a "Norbury rule" was proposed for the thermal conductivity in intermediate phases as an equivalent of the Norbury rule found for the electrical resistivity [3]. The method for predicting of intermetallic compounds with high thermal conductivity with main emphasis on the noble metals can be found in Ref. [4]. In our previous paper [5], we investigated the temperature dependences of all thermal properties of Fe_3Al-5at.%Cr with regards to the influence of phase transformation on the thermal conductivity. The measured stationary thermal conductivity of this intermetallic alloy is almost unaffected by $DO_3 \leftrightarrow B2$ transition. On the other hand, the temperature dependence of thermal diffusivity exhibits a peak in the transition range.

Ordered stoichiometric AuCu alloy exists in two modifications, tetragonal AuCu(I) and orthorhombic AuCu(II) forms. The AuCu(I) $\leftrightarrow$ AuCu(II) (order--order) temperature is accepted to be $385 \pm 2\,℃$ [7]. At higher temperatures, the transition AuCu(II) $\leftrightarrow$ AuCu(D) (order-disorder) occurs at the characteristic temperature of $410 \pm 2\,℃$ [7]. The AuCu(D) disordered phase has face centred cubic lattice.

The main purpose of this paper is to determine experimentally temperature dependence of the thermal diffusivity and thermal conductivity for ordered and disordered stoichiometric intermetallic AuCu alloy.

2. Experimental details

The AuCu alloy was prepared by induction melting of stoichiometric amounts of Cu and Au. Samples for the thermal diffusivity and thermal expansion measurements were spark-cut and their surfaces were polished using standard technique. The samples were annealed for one hour at $550\,℃$ in argon atmosphere and then water-quenched. For the quenched sample, a cubic lattice was determined by X-ray analysis. After high temperature measurement of the thermal diffusivity and

cooling of the sample in furnace, a tetragonal lattice was found with $c/a = 0.93$. By chemical analysis, 49.9 at.% of Au and 50.1 at.% of Cu was found in the alloy.

Thermal diffusivity was studied in the temperature range of 20–550 ℃ in argon atmosphere using a flash method described in Ref. [8]. The source of the light flash was a Xe-flash tube, duration of the pulse was 1 ms. The measurement at each temperature was performed after a 10 minute hold in order to start always from the equilibrium state. Several heat treatment cycles were applied to the sample. Each cycle consisted of a heating run, immediately followed by cooling in the furnace. The thermal diffusivity was measured with accuracy better than 3 %.

Linear thermal expansion was examined using the NETZSCH 402E dilatometer at temperatures from 20 to 550 ℃ in argon atmosphere. The diameter and length of the sample were 6 and 25 mm, respectively. The measurements were performed in the regime of linear heating with a rate of 5 ℃/min. The accuracy of the thermal expansion determination was of about 3 %.

Temperature dependence of the density was calculated from the density measured at 21 ℃ by weighing the sample in water and from respective values of volume thermal expansion measured up to 550 ℃.

3. Results and discussion

Figure 1 shows two temperature dependences of the thermal diffusivity. The 1^{st} run curve was obtained by measurement on the quenched sample, 2^{nd} one was estimated by measurement on the sample cooled in the furnace. The room temperature value of thermal diffusivity of the quenched sample was lower by one half than that for the further runs. The repeated runs exhibited the same course. The thermal diffusivity of quenched sample slowly increases up to 250 ℃ where an intense increase occurs. Above 400 ℃ there is a drop of the temperature dependence. The thermal diffusivity of the 2^{nd} run slowly increases up to 400 ℃ and then there is the same drop as it was in the 1^{st} run.

From Fig. 1, it can be seen that there is a large drop in the thermal diffusivity of AuCu at about 400 ℃ due to order-disorder phase transition. This large jump can be used to determine the characteristic temperature of the phase transition. The determination of the characteristic temperature was made by a method accustomed in resistometry [9], i.e. by derivation of the thermal diffusivity as a function of temperature. For the 2^{nd} run it is shown in Fig. 2 where we can see two minima. From their positions, the characteristic temperatures may be determined. The lower peak in Fig. 2 is due to the phase transition AuCu(I) $\leftrightarrow$ AuCu(II) with the characteristic temperature of 395 $\pm$ 3 ℃, the higher peak is caused by the phase transition AuCu(II) $\leftrightarrow$ AuCu(D) with the characteristic temperature of 410 $\pm$ 3 ℃. While the last temperature is in a good agreement with literature value [7], the characteristic temperature of AuCu(I) $\leftrightarrow$ AuCu(II) transition is about 10 ℃ higher. The position of the lower peak depends on the density of measured points.

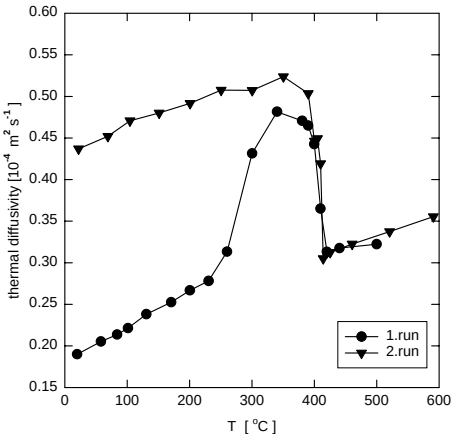

Fig. 1. Temperature dependence of thermal diffusivity of ordered and disordered AuCu alloy.

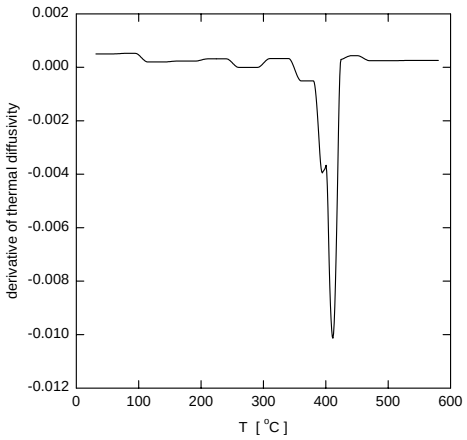

Fig. 2. Temperature dependence of the derivative of thermal diffusivity for 2$^{\mathrm{nd}}$ run.

The thermal conductivity was obtained as product of the thermal diffusivity, specific heat and density. The temperature dependence of the specific heat has been published recently [10] and the respective values were used for the calculation. The temperature dependence of the density was obtained as described in the experimental part. The estimated value of thermal conductivity at room temperature for the ordered alloy is 167 $\mathrm{W \cdot m^{-1} \cdot K^{-1}}$ which agrees with the literature value of 167 $\mathrm{W \cdot m^{-1} \cdot K^{-1}}$ [4]. The temperature dependence of the thermal conductivity for ordered and disordered alloy is shown in Fig. 3. The dashed segments in the figure indicate the temperature range close to the points of phase transitions, where the mentioned relation for the calculation of the thermal conductivity is not reliable and therefore has not been used.

In metals and alloys, the observed thermal conductivity is a sum of an electronic component λ_e and a lattice component λ_g [11],

$$\lambda = \lambda_\mathrm{e} + \lambda_\mathrm{g} \ . \tag{1}$$

Electronic thermal conductivity may be obtained from the Wiedemann-Franz law:

$$\lambda_\mathrm{e} = \frac{LT}{\rho} \ , \tag{2}$$

where ρ is the electrical resistivity, L is the Lorenz number (2.44×10^{-8} $\Omega \cdot \mathrm{m} \cdot \cdot \mathrm{K^{-2}}$) and T is the temperature.

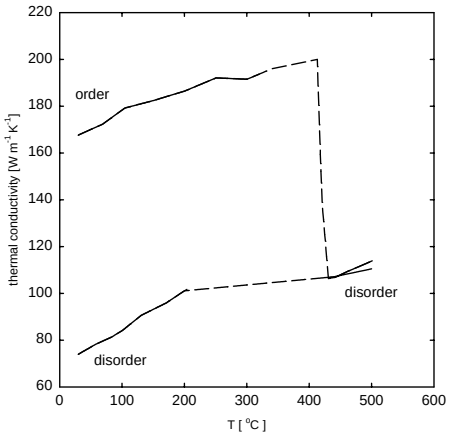

Fig. 3. Temperature dependence of the thermal conductivity for ordered and disordered AuCu alloy.

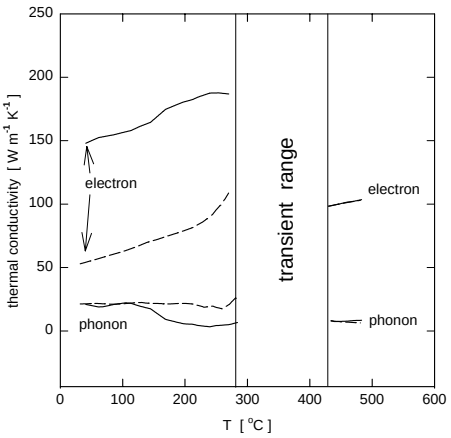

Fig. 4. Temperature dependence of the electronic and phonon thermal conductivity (—— ordered, – – disordered alloy).

Grube et al. [12] have found two-ordered state, designated as ordered a and ordered b state depending on the thermal history of the alloy. Because in our work the cooling rate was higher than 10 °C per 25 min, our results were compared with the electrical resistivity of the ordered b state (slower rate of cooling). The electrical resistivity of the ordered b state at room temperature was $5 \times 10^{-6}\,\Omega\cdot$m. Johansson and Linde [6] have reported a value of $5.7 \times 10^{-6}\ \Omega\cdot$m for the alloy cooled in a furnace. Using Grube et al. values [12] and our results, the electronic and phonon thermal conductivities were calculated. The temperature dependence of the electronic and phonon thermal conductivity is shown in Fig. 4. From this figure, it can be seen that the phonon thermal conductivity is approximately the same for the ordered and disordered state, whereas the electronic thermal conductivity is three times larger for the ordered state.

4. Conclusion

1. Values of thermal diffusivity and thermal conductivity of the ordered AuCu alloy are higher than those of the disordered alloy.

2. Using measurements of the thermal diffusivity, the characteristic temperatures of both AuCu(I) $\leftrightarrow$ AuCu(II) and AuCu(II) $\leftrightarrow$ AuCu(D) transitions were determined to be 395 ± 3 °C and 410 ± 3 °C, respectively.

Acknowledgements

The paper is dedicated to Professor Dr. Z. Trojanová on the occasion of her 60^{th} birthday. I am grateful to Dr. L. Dobiášová for the X-ray analysis.

REFERENCES

[1] XU, W.—SCHULSON, E. M.: Acta Metall. Mater., *43*, 1995, p. 2121.
[2] HANAI, S.—TERADA, Y.—OHKUBO, K.—MOHRI, T.—SUZUKI, T.: Intermetallics, *4*, 1996, p. 41.
[3] TERADA, Y.—MOHRI, T.—SUZUKI, T.: Mat. Res. Soc. Symp. Proc., *364*, 1995, p. 201.
[4] TERADA, Y.—NAKATA, J.—MOHRI, T.—SUZUKI, T.: Intermetallics, *6*, 1998, p. 479.
[5] RUDAJEVOVÁ, A.—ŠÍMA, V.: Mat. Res. Bull., *22*, 1997, p. 441.
[6] JOHANSSON, C. H.—LINDE, J. O.: Ann. Phys., *25*, 1936, p. 1.
[7] Binary Alloy Phase Diagrams. Editor-in-chief: Masalski, T. B. ASM International, Materials Park, Ohio 1996, p. 358.
[8] RUDAJEVOVÁ, A.: Mat. Res. Bull., *26*, 1991, p.1363.
[9] SPRUŠIL, B.—ŠÍMA, V.—CHALUPA, B.—SMOLA, B.: Z.Metallkd., *84*, 1993, p. 2.
[10] ŠÍMA, V.: J. Chim. Phys., *90*, 1993, p. 451.
[11] KLEMENS, P. G.: Solid State Physics. Eds.: Seitz, F., Turnbull, D. New York, vol. 7, 1958, p. 1.
[12] Von GRUBE, G.—SCHOMANN, G.—VAUPEL, F.—WEBER, W.: Zeits. f. anorg. Chemie, *201*, 1931, p. 41.

Received: 29.5.2002
Revised: 16.7.2002