Low frequency internal friction spectra of $\text{Cu}_{0.81}\text{Pd}_{0.19}$ alloy

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Abstract. Results on the internal friction of disordered and partially ordered $\text{Cu}_{0.81}\text{Pd}_{0.19}$ alloy in the temperature range 160–300 K and frequency range 1–2 Hz are reported. All the peaks are classified into three groups. Two prominent peaks of the first group occurring between 180 and 200 K are observed only in completely disordered samples. A long annealing treatment removes these peaks. These peaks may be due to interaction of dislocations with preferentially clustered palladium atoms in the disordered alloy. A second group of peaks in the temperature range 210–270 K is sensitive to the microstructure and are presumably related to dislocation–dislocation interactions. In partially ordered samples new peaks appear at between 210 and 285 K. Activation parameters of these peaks are presented.

Keywords. Internal friction; mechanical properties; copper–palladium alloy.

1. Introduction

The internal friction of a crystalline material is sensitive to the defect state comprising of point defects, line defects, or local deviations of atomic structure and interactions of the defects among themselves. Although a selective tool in probing atomic movements or relaxations via defects, it appears the technique has yet to be fully exploited towards investigating various defect mechanisms in the crystalline state. It is well known that cold-worked *fcc* metals show Hasiguti peaks due to the interaction of intrinsic point defects and dislocations for temperatures between 77 and 300 K (Hasiguti 1972). In dilute alloys of *fcc* metals based on copper and aluminium several investigators (Iwasaki *et al* 1975, 1980; Koiwa *et al* 1975; Iwasaki 1977) have reported Hasiguti peaks due to interactions of dislocations and solute atoms or solute atom point defect complexes. In going over to concentrated metallic alloys of *fcc* metals the peaks are found to be poorly reproducible and show strong dependence on sample treatment. Several aspects of internal friction in the case of concentrated alloys remain obscure and warrant investigations as evident from the works of Iseki *et al* (1977), Iwasaki (1981), Kong *et al* (1981) and Othmezzouri-deCerf (1983). Besides in the case of alloys that form ordered structures, it would be interesting to see how the degree of order and the type of the ordered lattice affect the internal friction. The copper–palladium alloy chosen here has interesting structural features and its internal friction spectrum has not been investigated in any detail. In this paper, we report results of our experimental studies on $\text{Cu}_{0.81}\text{Pd}_{0.19}$ in the temperature range 160–300 K and for low frequencies of 1–4 Hz.

2. Experimental method

The material in the form of wire of diameter 0.8 mm was acquired from M/s Johnson Matthey Metals Ltd. The composition of the material was confirmed by

electron probe microanalysis. For the purpose of annealing, the wires were placed in quartz tubes evacuated to better than 10^{-4} torr and sealed. Two forms of heat treatment were given:

- (a) Annealing at 1073 K for 3 h and cooling slowly to room temperature over a period of 3 days. These samples will be referred to as SA samples.
- (b) Another set of samples were cooled from 1073 K to 743 K at a rate of 30–50 K every 5 hr. The samples were then annealed for a period of 20 days at 743 K and cooled in the furnace slowly. This set of samples will be referred to as LA samples.

The internal friction was recorded on as-received (AR), SA and LA samples using an inverted torsion pendulum equipment operating between frequencies 1–4 Hz and temperatures 100–300 K in the free decay mode (Sobha *et al* 1986).

The samples were aged under vacuum at 300 K *in situ* between successive experimental runs. The mean heating rate adopted was 1 K/min and the temperature difference across the sample was always within 5 K. The maximum strain amplitude acting on the outer fibres of the specimen was always 10^{-5} . All the experimental runs were conducted under a vacuum of 10^{-4} Torr or better.

2.1 X-ray analysis

The lattice parameters were estimated from Debye–Scherrer photographs. The AR and SA samples showed a disordered *fcc* lattice with good agreement of lattice parameters. The LA samples showed partial ordering as evidenced by two superlattice lines corresponding to Bragg angles 24.396° , 27.39° on the front reflection side. The two lines could be indexed as (120_T) and (200_T) of a pseudo-*fcc* lattice. Table 1 lists the lattice parameter data.

2.2 Methods of analysis

Two methods as outlined below were adopted for analysis:

- (a) A given peak is decomposed into two or three components by single reflection and subtraction following Klam *et al* (1979). The components so resolved are then fitted by the method of least squares to the equation:

$$Q^{-1} = 0.5 g \operatorname{sech} [(1/T) - (1/T_p)] W/k], \quad (1)$$

where g is the relaxation strength and T_p is the peak temperature. The first peak is indicated as C_n , a main peak, and the second is denoted with a second subscript s . Figures 1 and 2 illustrate such a decomposition for C_4 (SA) and a typical computer fit, respectively.

Table 1. Lattice parameters a and c (nm) of $\text{Cu}_{0.81}\text{Pd}_{0.19}$ alloy after various treatments.

Sample	a	c	c/a	Reference
As-received (AR)	0.3675	—	—	Present work
Disordered alloy	0.3673	—	—	Hansen and Anderko (1958)
Long annealed (LA)	0.3679	0.3643	0.990	Present work
Short annealed (SA)	0.3673	—	—	Present work

Figure 1. Two-component fit of C_4 of an SA sample.

Figure 2. Least squares fit of the resolved component of C_4 .

(b) Each of the component peaks is assumed to have a lognormal distribution of relaxation times. To find the half-width of the distribution a parameter X is defined:

$$X = (1/2.303) [\ln(f(T)/f_p) + (W/k)((1/T) - (1/T_p))] \quad (2)$$

where $f(T)$ is the frequency at the temperature T , f_p is the frequency at the peak temperature. The normalised Q^{-1} is plotted as a function of X . The halfwidth parameter at different temperatures was obtained by comparison with the values tabulated by Nowick and Berry (1972). Figure 3 illustrates the application of this method for C_3 .

Figure 3. Lognormal distribution fit for C_3 of SA sample.

3. Microstructure

The copper–palladium binary alloy forms one- or two-dimensional long period superstructures for compositions around the stoichiometric ratio 3:1.

In quenched samples of the $\text{Cu}_{0.79}\text{Pd}_{0.21}$ alloy, Tanaka and Ohshima (1984) observed ordered regions floating in a disordered matrix. Guymont and Gratias (1976) noted the formation of a long period superstructure which transforms to an L1 structure subsequently. A periodic antiphase structure develops along $\langle 100 \rangle$ in samples annealed at 723 K for 5 days. The TEM and HREM studies of Brodin *et al* (1986) confirmed the occurrence of one-dimensional long period superstructures and diffuse anti-phase domain boundaries. These findings are relevant for our long-term annealed samples (LA). The AR and SA samples on the other hand have a completely disordered *fcc* lattice, the former being in addition heavily deformed. The LA samples have partially ordered regions in a disordered matrix, with a residual density of line defects.

4. Results and discussion

The internal friction and the modulus defect represented by the oscillation frequency are shown in figures 4–9 for AR, SA and LA samples for different runs (see also table 2). Following are the salient features of the spectra:

- (i) the background damping is high in as-received wires and decreases considerably on annealing;
- (ii) the peaks below 210 K occur only in AR and SA samples. Evidently the longer duration of annealing adopted in LA samples has eliminated the structural defects responsible for peaks below 210 K. We classify them under group I;
- (iii) in the temperature range of 210–270 K peaks occur in all three types of samples. These peaks fall in group II. Noticeable differences in the spectra of SA and LA samples in this temperature range shows that there is a large influence of microstructure modification;
- (iv) in only LA samples, peaks occur above 270 K.

These constitute group III.

Figure 4. Internal friction and modulus defect of AR sample of $\text{Cu}_{0.81}\text{Pd}_{0.19}$ alloy.

Figure 5. Internal friction and modulus defect of SA sample of $\text{Cu}_{0.81}\text{Pd}_{0.19}$ alloy (first run).

Figure 6. Internal friction and modulus defect of SA sample of $\text{Cu}_{0.81}\text{Pd}_{0.19}$ alloy (second run).

Figure 7. Internal friction and modulus defect of SA sample of $\text{Cu}_{0.81}\text{Pd}_{0.19}$ alloy (third run).

Figure 8. Internal friction and modulus defect of LA sample of $\text{Cu}_{0.81}\text{Pd}_{0.19}$ alloy (first run).

Figure 9. Internal friction and modulus defect of LA sample of $\text{Cu}_{0.81}\text{Pd}_{0.19}$ alloy (second run).

Table 2. Prominent internal friction peaks in $\text{Cu}_{0.81}\text{Pd}_{0.19}$.

Peak symbol (sample type)	Temperature and frequency	Group
C_1 (AR)	199 K, 1.96 Hz	I
C_6 (SA)	199 K, 1.77 Hz	I
C_3 (SA)	184 K, 1.81 Hz	I
C_{6s} (SA)	206 K, 1.73 Hz	I
C_4 (SA)	227 K, 1.75 Hz	II
C_{4s} (SA)	215 K, 1.78 Hz	II
C_8 (SA)	265 K, 1.7 Hz	II
C_{8s} (SA)	278 K, 1.7 Hz	II
C_{10} (SA)	240 K, 1.67 Hz	II
C_{12a} (LA)	230 K, 2.39 Hz	II
C_{12b} (LA)	215 K, 2.39 Hz	II
C_{12c} (LA)	253 K, 2.24 Hz	II
C_{13} (LA)	282 K, 2.28 Hz	III
C_{13s} (LA)	286 K, 2.28 Hz	III

4.1 Group I

Two prominent peaks occur at 199 [C_1 , C_6] and 184 K [C_3 , C_{15}]. The peak at 184 K is seen to be a pure Debye peak. As seen in table 3 the activation energies are generally similar to the values known for the Hasiguti peak P_b reported by Iwasaki (1975) in other copper-based alloys. Accordingly we tend to attribute this peak to interactions of dislocations with solute atom clusters. Since the palladium atom is oversized with respect to copper (7%), hardening can result. The rigidity modulus of palladium is less than that of copper (16%). Palladium may thus act as soft pinning in copper and may have an attractive interaction with a dislocation and its stress field relieved by preferential migration of Pd atoms towards them.

4.2 Group II

The peak C_2 (AR), peaks C_4 , C_{4s} , C_8 and C_{10} , all occurring in SA samples, and the peaks C_{12a} , C_{12b} , C_{12d} , identified in LA samples, come under this group. The activation parameters are shown in table 3.

The peak C_{12a} and its shoulder show features characteristic of a thermally activated relaxation process. They exhibit a uniform distribution of relaxation values. The peak C_8 (SA) at 266 K also repeats as C_{11} (SA) in a successive run. The peak C_{8s} (SA) falls in height and gets resolved from the main peak in the third run. Also we identify the sharp peak C_3 (SA) which should correspond to C_{8s} (SA). From the analysis of lognormal distribution, it is evident that the peak C_8 of SA samples has a distribution of Debye peaks. The prominent peak C_{10} at 240 K has a corresponding peak C_2 in AR samples with a larger strength and modulus defect as expected in view of the magnitude of presumed deformations in them. It may be seen from table 3 that the activation parameters for some peaks in the SA samples are abnormal. However such abnormal values seem to be generally observed in concentrated alloys as in the works of Iseki *et al* (1977) on $\text{Cu}_{0.85}\text{Al}_{0.15}$,

Table 3. Activation parameters of prominent internal friction peaks in $\text{Cu}_{0.81}\text{Pd}_{0.19}$ alloy.

Peak symbol (sample type)	Activation energy W (eV)	Pre-exponential factor (s)	Group
C_1 (AR)	0.63	7.98×10^{-18}	I
C_6 (SA)	0.69	2.35×10^{-19}	I
C_3 (SA)	0.99	5.53×10^{-29}	I
C_{6s} (SA)	0.66	7.18×10^{-18}	I
C_4 (SA)	1.6	3.72×10^{-37}	II
C_{4s} (SA)	1.78	4.00×10^{-30}	II
C_8 (SA)	1.33	5.59×10^{-27}	II
C_{8s} (SA)	1.54	1.40×10^{-29}	II
C_{10} (SA)	1.47	1.45×10^{-32}	II
C_{12a} (LA)	0.75	2.63×10^{-18}	II
C_{12b} (LA)	0.92	2.75×10^{-23}	II
C_{12c} (LA)	0.90	9.14×10^{-28}	II
C_{13} (LA)	3.94	3.8×10^{-72}	III
C_{13s} (LA)	2.71	2.26×10^{-49}	III

Iwasaki (1981) on Cu–Zn and Cu–Ni alloys and Kong *et al* (1981) on $\text{Au}_{0.75}\text{Cu}_{0.25}$. Koiwa (1977) developed a model of interacting anelastic elements which leads to apparently large activation energies and pre-exponential frequency parameters. It is therefore possible that the peaks cited above may arise from interacting line defects in the disordered samples.

In LA samples three clear peaks C_{12a} , C_{12b} , C_{12d} occur at 230, 215 and 253 K replaced in the second run by a sharp peak C_{15a} at 256 K. Schlipf's model (1985) of thermally activated motion of dislocations in concentrated alloys encountering clusters of atoms forming obstacles of differing strengths seems to be relevant here for these peaks. It should be noted that these samples do contain both ordered and disordered regions but it is the disordered matrix presenting a random array of point defects to dislocation motion that presumably is responsible for the peaks.

4.3 Group III

Peaks C_{13} , C_{13s} and C_{14} , all in LA samples, fall in this group. We identify peak C_{14} as C_{13} shifted by 10 K on the high temperature side in a successive run. Buynova *et al* (1970, 1972), Yasyreva and Yakovleva (1974) reported TEM studies on completely ordered copper–palladium alloys plastically deformed. In the early stages of deformation, planes of disturbed long range order easily form when the superdislocation intersects a domain wall. Thus we associate this group with dislocations of the partially ordered domains in such a defect state. Muira *et al* (1981) and Muira (1985) reported a maximum in the damping of $\text{Cu}_{0.75}\text{Pd}_{0.25}$ alloys for intermediate long range order.

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