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STUDY OF ORDER–DISORDER TRANSFORMATION OF COPPER–GOLD ALLOYS BY MEANS OF DIFFERENTIAL THERMAL ANALYSIS

P. TISSOT AND R. DALLENBACH

Département de chimie Minérale, Analytique et Appliquée, Université de Genève, 30, quai Ernest Ansermet, 1211 Genève 4 (Switzerland)

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ABSTRACT

Several copper-gold alloys, with compositions of between 10 and 80 atomic percent of gold, were examined by quantitative DTA from 25 to 500°C. The results are in good agreement with those obtained by other less rapid, but more accurate, methods. All the reactions observed were first-order transformations. A latent heat (180 ± 40 cal g-at^{-1}) was measured at 405°C for the $\alpha_I'' \rightarrow \alpha_{II}''$ transformation of the alloy containing 50% of gold. An endothermic effect, corresponding to an order–disorder reaction, was detected for all alloys, up to a composition of over 90 atomic percent of gold.

INTRODUCTION

An abundant literature has been devoted from many years to the study of order–disorder transformations, but it is clear that differential thermal analysis (DTA) is a technique not often used[1–5]. As indicated by Castenet and Urbain[6], this method is interesting because complete information on the structural transformations of an alloy may be rapidly obtained. However, this dynamic method can only be used to study phenomena which are sufficiently rapid with respect to the heating rate used.

EXPERIMENTAL

We have studied the well known copper–gold system, which shows a continuous substitution solid solution (α_D) and many ordered phases (α', α_I'', α_{II}'', α''') (see Fig. 1). All the solid state transformations take place between 200 and 400°C. All measurements were made using a Mettler quantitative DTA apparatus, type TA 2000. Samples were prepared by melting copper and gold (Balzer Coating Quality, 99.99%) in graphite crucibles. Sample weights were 50 ± 2 mg for compositions over 65 atomic percent (at %) copper, and 980 ± 20 mg for compositions lower than 65 at % copper. For thermal analysis, aluminium crucibles were used, and the

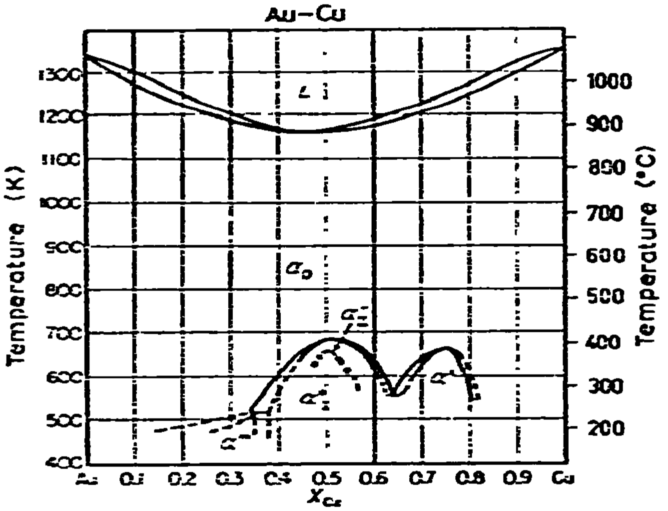

Fig. 1. The copper–gold system[7].

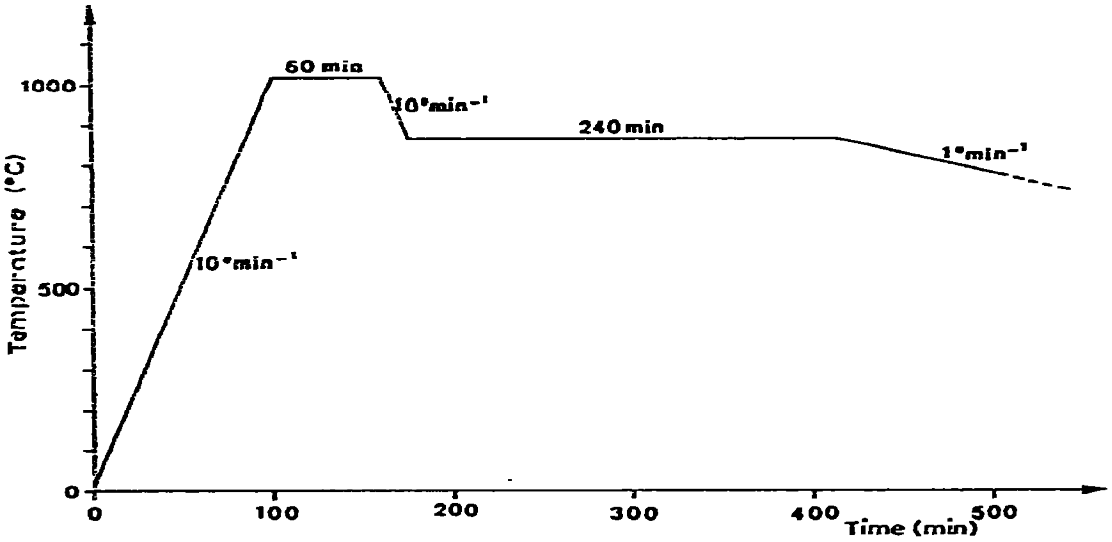

Fig. 2. Heating treatment used for the preparation of samples.

reference was the same weight of pure gold; the heating rate was 4 deg min^{-1}. Preparation of alloys, thermal treatments and differential thermal analysis were performed under a nitrogen atmosphere (99.995%). The formation of an ordered phase is generally assumed to proceed by nucleation and growth. This mechanism leads to the formation of antiphase domains, the slow growth of these domains being the limiting factor of the degree of order. The method of preparation of the samples is thus very important, and we used the treatment indicated in Fig. 2, which seems to give the best resolution and reproducibility of DTA peaks. The small spheres obtained were then pressed between two steel plates to make a flat surface of 1 mm, to ensure good contact with the aluminum crucible. The composition of the alloys was checked by neutron activation and analysis of ^{66}Cu and ^{198}Au content. All the heat treatments were performed under nitrogen, in Pyrex tubes heated in a small electrical furnace.

RESULTS AND DISCUSSION

In order to determine the optimum duration of annealing to obtain ordered alloys, we quenched a line of samples AuCu and $AuCu_3$ beginning at 450°C. These samples were annealed at 370°C for different periods. Some DTA curves obtained are shown in Fig. 3. We observe an evolution of the peak shape, of the area and of the temperature, all as functions of the annealing time. This evolution is particularly striking for AuCu, for which the first peak, corresponding to the transformation $\alpha_I'' \rightarrow \alpha_{II}''$ appears only after an annealing time of several minutes at 370°C; the second peak, corresponding to the transformation $\alpha_{II}'' \rightarrow \alpha_D$, is doubled when the annealing lasts less than ten hours. We have never observed an evolution after 24 hours at 370°C, and we decided to anneal each sample for at least 60 hours at a temperature 10 degrees below the transformation temperature. For transitions occurring at temperatures below 220°C, the thermal treatment was extended to 100 hours.

We have also studied the influence of the heating rate, between 2 and 15 deg min^{-1}, on the temperature and the area of the peaks. We observed a steady increase in the temperature; on the other hand, the peak area remains roughly constant. For the alloys near AuCu, which present two peaks, we also observed a constant total area, although the first peak increases and the second decreases with increasing heating rate. We chose, for all DTA measurements, a heating rate of 4 deg min^{-1}.

In Table 1, we list the onset- and maximum-peak temperature for all the samples. These results can be divided in three groups, corresponding to the composi-

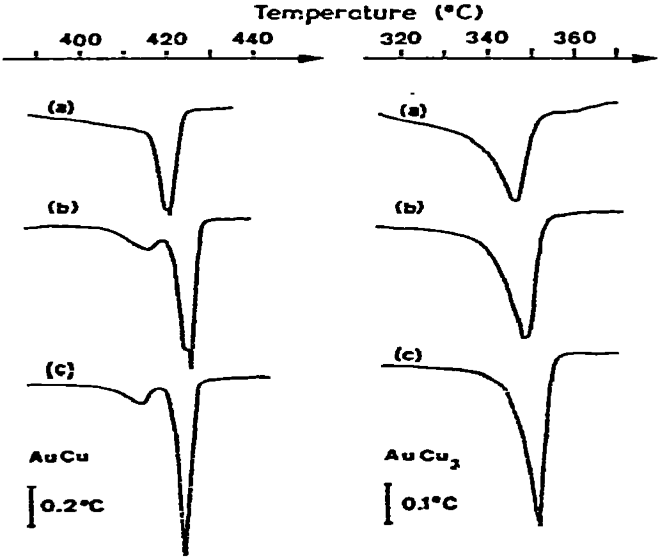

Fig. 3. Influence of the annealing duration.

TABLE I

PEAK TEMPERATURES AND ΔH VALUES OF THE ORDER–DISORDER REACTION

at % Cu	*Peak temperature (°C)*		$\Delta H_{(o\to d)}$ *(cal g-at^{-1})*
	Onset	*Maximum*	
10	210	230	5
15	200	230	19
20	190	230	45
25 (Au_3Cu)	190	235	172
30	210	240	200
35	215	245	205
40.5	330	345	156
42.7	320/362	357/376	35/207
44.3	330/378	367/384	50/290
46.4	340/402	395/411	82/290
48.6	370/419	415/425	157/328
49.9 (AuCu)	388/421	418/432	180/385
51.9	402/419	415/427	190/360
54.1	365/405	399/418	50/303
56.9	360	388	255
59.9	325	360	228
69.1	335	365	169
71.1	337	376	197
72.4	372	398	226
74.5 ($AuCu_3$)	380	394	289
77.1	360	387	250
79.2	325	340	239

tions on either side of each ideal composition Au_3Cu, AuCu and $AuCu_3$. The curves obtained for each group are shown in Figs. 4, 5 and 6. The temperatures of the superlattice boundaries (see Fig. 1) are indicated on each curve; the agreement is quite good, and it is clear that DTA affords rapidly, and to a good degree of approximation, the general appearance of the order–disorder transformations of this binary system. In all cases, the shape of the peaks is characteristic of a first order transformation. The difference between first and second order transformations is clearly demonstrated by comparison with Fig. 7, which illustrates, the transformation of the β phase of the alloy Cu–Zn, which is considered to proceed by a second order reaction [8,9].

The peaks of the gold-rich alloys (Fig. 4) are quite broad, due to the relatively low temperature of the transformation and to the sample weight (~ 1 g). Within our experimental conditions, the transformation extends over 40–50 degrees, equivalent to 10 minutes at a heating rate of 4 deg min^{-1}. The enthalpy variation measured for Au_3Cu ($\Delta H_{(o\to d)}$ = 172 cal g-at^{-1}) is in good agreement with the calorimetric measurements of D'Heurle and Gordon[10] who report a value of 180 cal g-at^{-1} for an alloy quenched from 500 to 187 °C. No maximum value is observed for the ideal composition Au_3Cu. We have measured a thermal effect until 90 at % gold, although Battermann[11], using X-ray analysis, did not observe a superstructure with alloys richer than

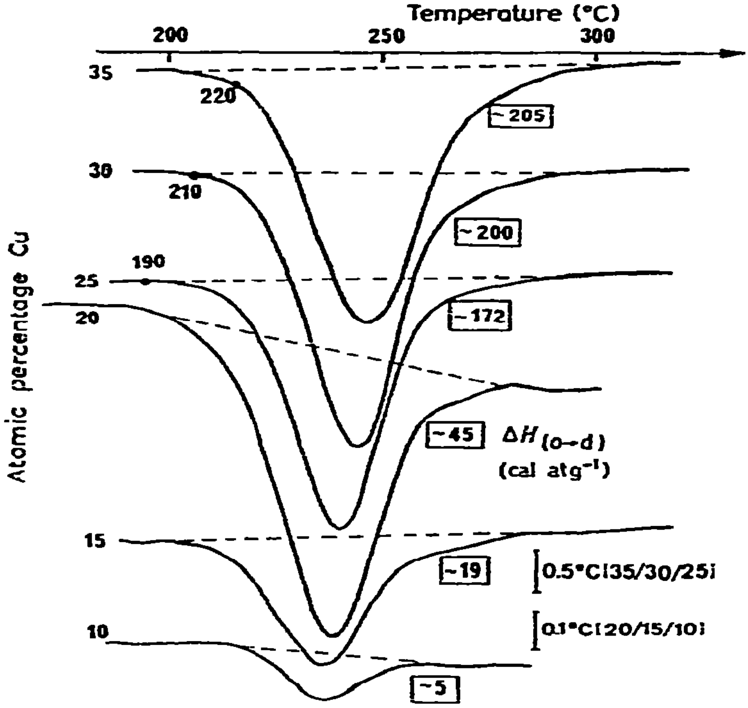

Fig. 4. DTA curves near Au_3Cu.

75 at % gold. The alloys near AuCu (Fig. 5) show two peaks. The smaller corresponds to the transformation $\alpha_I'' \to \alpha_{II}''$; the larger, very sharp peak, corresponds to the formation of the disordered alloy. According to theory, the enthalpy variation decreases on either side of the ideal composition AuCu (see Fig. 8), where the degree of order is at a maximum. Figure 9 depicts the enthalpy variation of formation for AuCu as a function of temperature[7]. This value varies progressively up to 410°C; no-one has yet succeeded in showing the presence of a jump near 380°C, which may correspond to the transformation $\alpha_I'' \to \alpha_{II}''$. At 410°C, the ΔH value is 390 cal g-at^{-1}. Figure 9 also shows the values obtained by DTA. Between 385 and 435°C, two jumps are observed: the first one (405°C, 180 cal g-at^{-1}) corresponds to the transformation $\alpha_I'' \to \alpha_{II}''$; the second one (420°C, 385 cal g-at^{-1}) corresponds to the transformation $\alpha_{II}'' \to \alpha_D$. We have calculated for these two reactions the values $\Delta S = 0.27$ and $\Delta S = 0.56$ cal g-at^{-1} deg^{-1}, respectively. All these values are in good agreement with those indicated in the literature[7]. Copper-rich alloys (Fig. 6) also show a maximum of enthalpy variation for the ideal composition $AuCu_3$ (Fig. 8). As before, we compared the enthalpy of formation of $AuCu_3$ with the results obtained in this work (Fig. 10): our measurements agree quite well with those reported in the literature[7], and the calculated variation of entropy is $\Delta S = 0.44$ cal g-at^{-1} deg^{-1}. For all compositions, good reproducibility during several successive thermal treatments and DTA measurements was, in general, observed. This means that the growth of antiphase domains does not play an important role; on the other hand, the effects measured by DTA represent the establishment of surstructure in each antiphase domain.

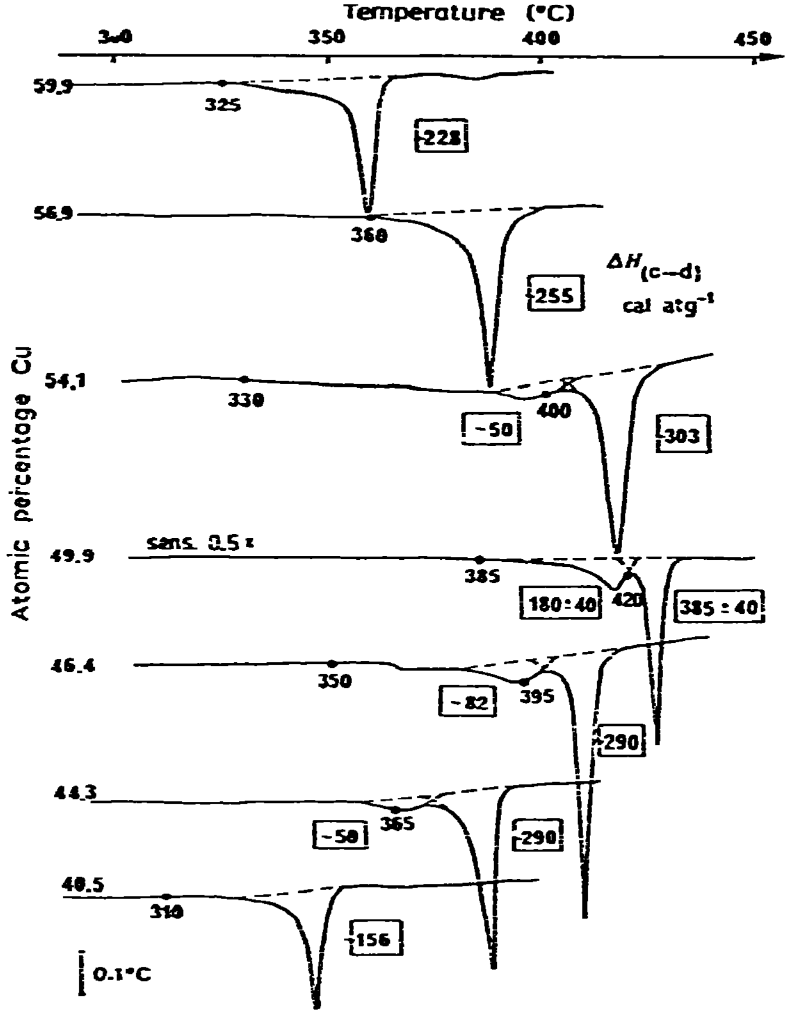

Fig. 5. DTA curves near AuCu.

We have also studied the reversibility of the order–disorder reaction during several successive heating and cooling cycles. In the case of Au_3Cu, the transformation is practically irreversible under these conditions. During the cooling, we did not observe any thermal effect, and during the second heating, only a very small endothermic peak was observed. The results obtained with AuCu and $AuCu_3$ are shown in Figs. 11 and 12. For AuCu, we observe the disappearance of the first peak on the cooling curve; it does not appear again during the successive heating, but the second peak shows a double maximum. The reaction disorder → order seems to be more rapid or complete than the reverse reaction, as shown by the higher value of ΔH observed during the cooling. In the case of $AuCu_3$, the thermal effects on cooling and heating are approximatively the same after the first cycle.

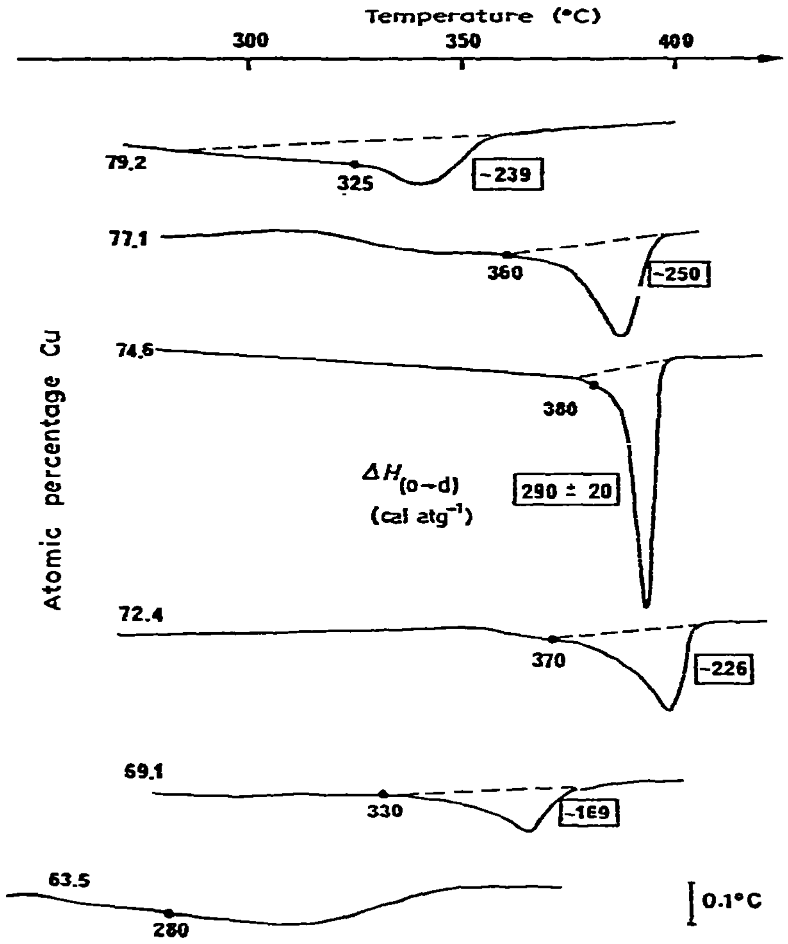

Fig. 6. DTA curves near $AuCu_3$.

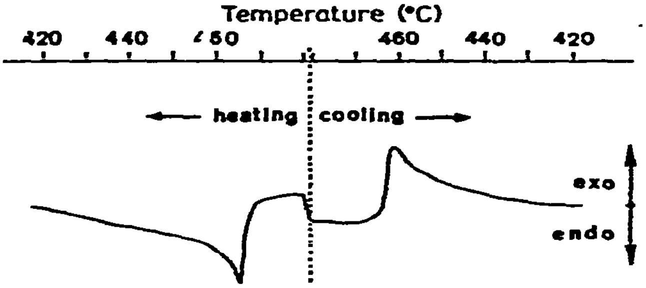

Fig. 7. DTA curves for β-brass: sample, 26 mg, 47 at % Zn; reference, 50 mg, pure copper.

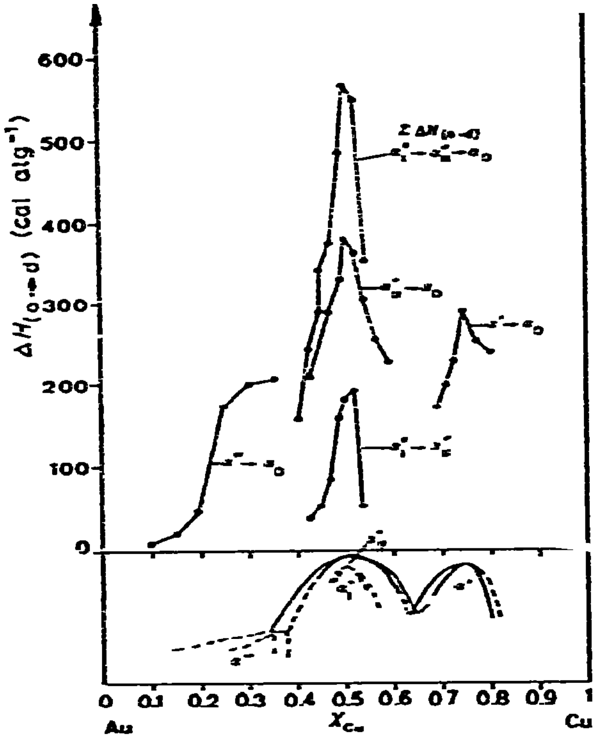

Fig. 8. ΔH values obtained by DTA for the reaction order→disorder in the copper–gold system.

Fig. 13 shows two curves obtained with alloys quenched in cold water from 450°C. The formation of surstructure begins near 60°C. At 350°C, the speed of order formation diminishes, and the disappearance of order takes place. The area on each side of the base line gives the following results:

AuCu $H_{(d\to o)}$: -490 cal g-at^{-1}
$H_{(o\to d)}$: 315 cal g-at^{-1}
$AuCu_3$ $H_{(d\to o)}$: -560 cal g-at^{-1}
$H_{(o\to d)}$: 205 cal g-at^{-1}

The difference observed between the two reverse reactions may be attributed to the formation of short range order, which does not disappear during the formation at the disordered phase α_D[12].

CONCLUSIONS

The use of a sensitive DTA device, such as the Mettler TA 2000, is very useful for studying the phase transformations of materials. One of the advantages is the rapidity of measurement, although the accuracy is not very high. With this technique, we have shown all the known transformations of the system copper–gold; we have clearly demonstrated that all these transformations are first-order reactions and have determined the associated ΔH values. Finally, we have studied the reversibility of

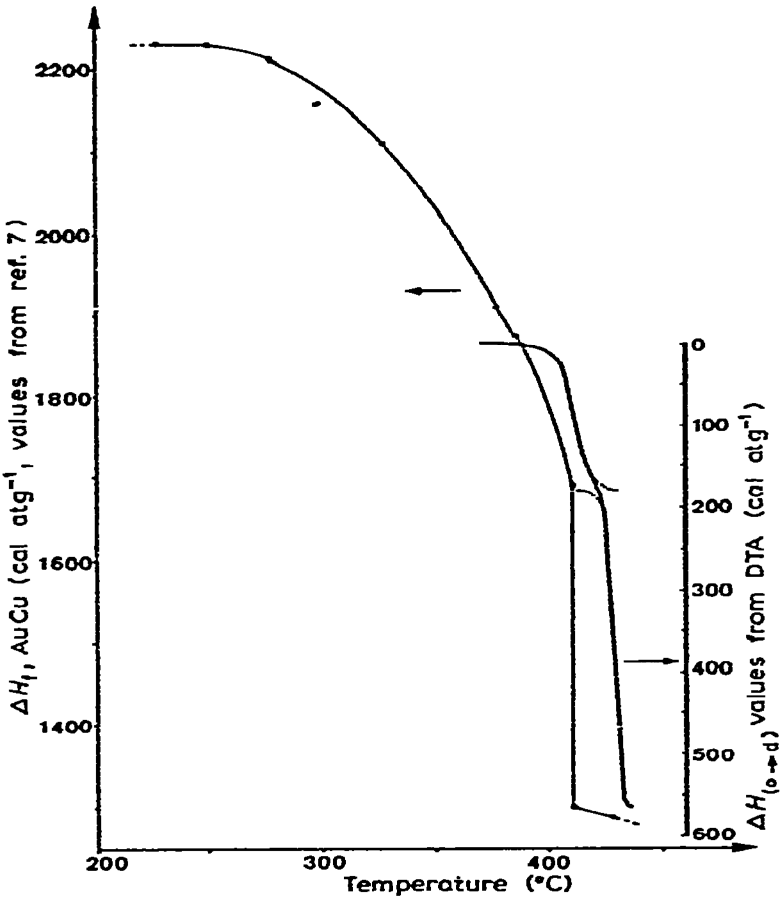

Fig. 9. — ΔH_f and $\Delta H_{(o\to d)}$ as a function of temperature for AuCu.

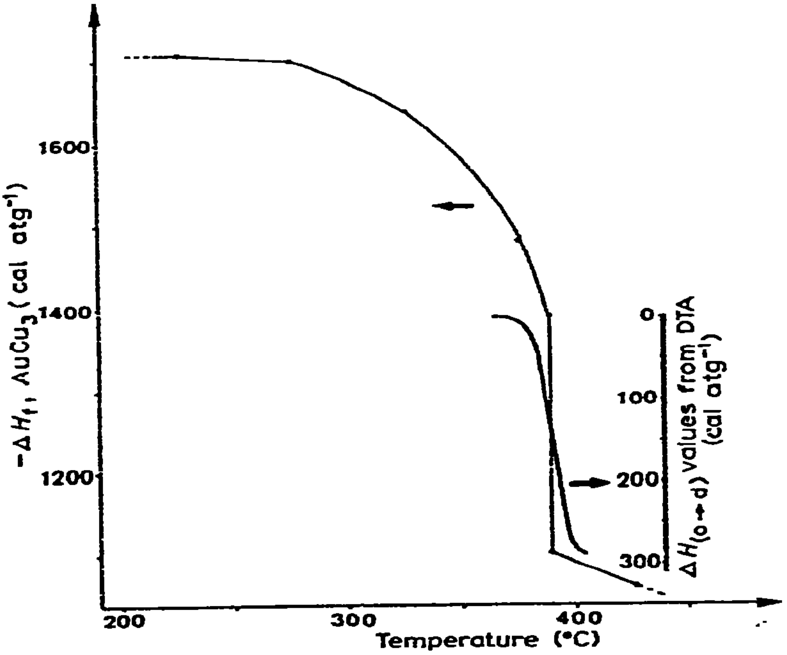

Fig. 10. — ΔH_f and $\Delta H_{(o\to d)}$ as a function of temperature for AuCu$_3$.

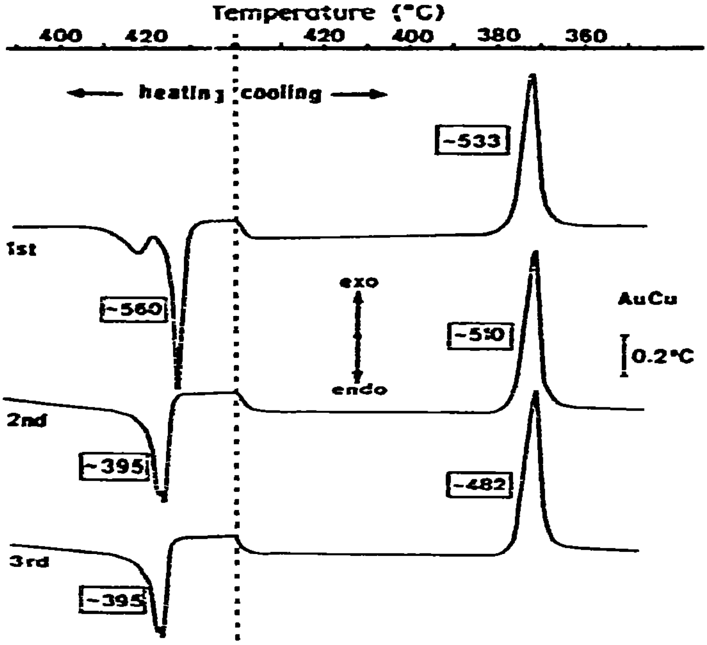

Fig. 11. Reversibility of the transformation for AuCu.

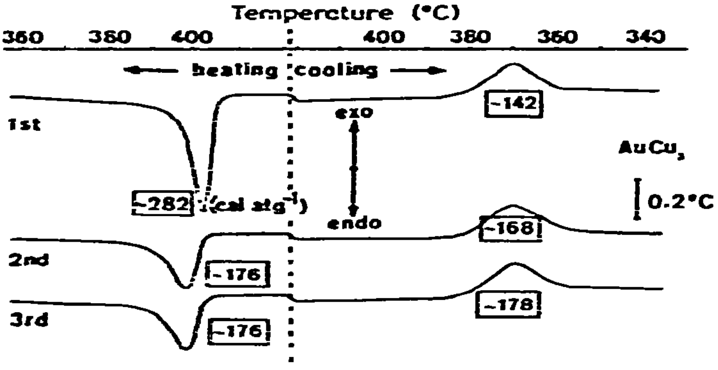

Fig. 12. Reversibility of the transformation for AuCu₃.

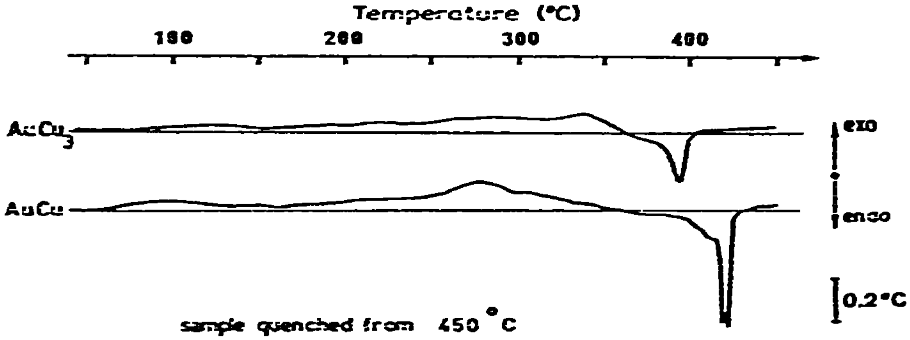

Fig. 13. DTA curves obtained with quenched alloys.

some of these transformations; DTA allows one to show the difference between AuCu and $AuCu_3$. In particular, the transformation $\alpha_I \rightarrow \alpha''_{II}$ appears to be completely irreversible within our experimental conditions.

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