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Differential thermal analysis and structure of the Ni-TiC system

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The sintering processes of Ni–TiC powder mixtures with the addition of a third alloying element, Mo, Ta or Co, were studied by differential thermal analysis and optical microscopy at room temperature and high temperature. The TiC content was varied between 5 and 90 wt%, and Mo, Ta and Co contents were varied between 0 and 20 wt%. The mean TiC powder and metal powder sizes were 1 and 2 μm, respectively. The initiation of a endothermic reaction was observed by thermal analysis of the Ni–TiC system. The structural change corresponding to the reaction was confirmed by optical microscopy.

1. Introduction

Nickel and its alloys which have been strengthened by titanium carbide particles have been much investigated due to their good friction and heat resistance properties [1, 2] and the phase diagrams of Ni–Ti–C have been established [3, 4].

It has been stated that the sintering temperature and time are very important in the powder metallurgical preparation of Ni–TiC alloys [5], and some work on the sintering process and wettability between nickel and titanium carbide have also been reported [6–8]. The reaction of a Ni–TiC powder mixture has been studied by microstructural observations and X-ray techniques [9].

The present work was performed to clarify the reaction of the Ni–TiC powder mixture in the Ni–TiC system blended with fine powders of Mo, Ta and Co during the sintering process. Differential thermal analysis was used to define the high temperature reactions and to observe the structural changes corresponding to these reactions.

2. Experimental procedure

A series of Ni–TiC powder mixtures were prepared by using Ni powder of 2 μm mean particle size and 5 to 90 wt% TiC powder of 1 μm mean particle size. Other mixtures were prepared by adding other elements such as Mo, Ta and Co individually to Ni with a fixed percentage of TiC. Differential thermal analyses were performed on these powder mixtures; 0.5 g of the powder mixture was taken for one measurement and aluminium oxide powder was used as the standard sample.

The specimens were set in a vacuum of 10^{-3} torr and differential thermal analysis was carried out in the temperature range room temperature to about 1400° C at a heating rate of 3.5° C min^{-1}. A Pt–PtRh thermocouple was used to measure and control the temperature.

Three samples of the Ni–TiC system, containing 30, 40 and 70 wt % titanium carbide were quenched at a rate of 100° C sec^{-1} from the temperature which was considered to be important from the differential thermal curve.

Ni–30 wt % TiC powder was pressed at 2 ton cm^{-2} (196.13 MPa) and the microstructure at high temperature was observed using a Union Co. HM-4 type high temperature microscope. During the microscopic observations, argon gas flowed at a rate of 0.1 l min^{-1} in order to protect the lens from frosting.

The Pt–PtRh thermocouples were set below the compressed powder specimens of 10 mm diameter and 2 mm thickness. The specimens were heated at a rate of 2° C min^{-1} from room temperature to about 1400° C.

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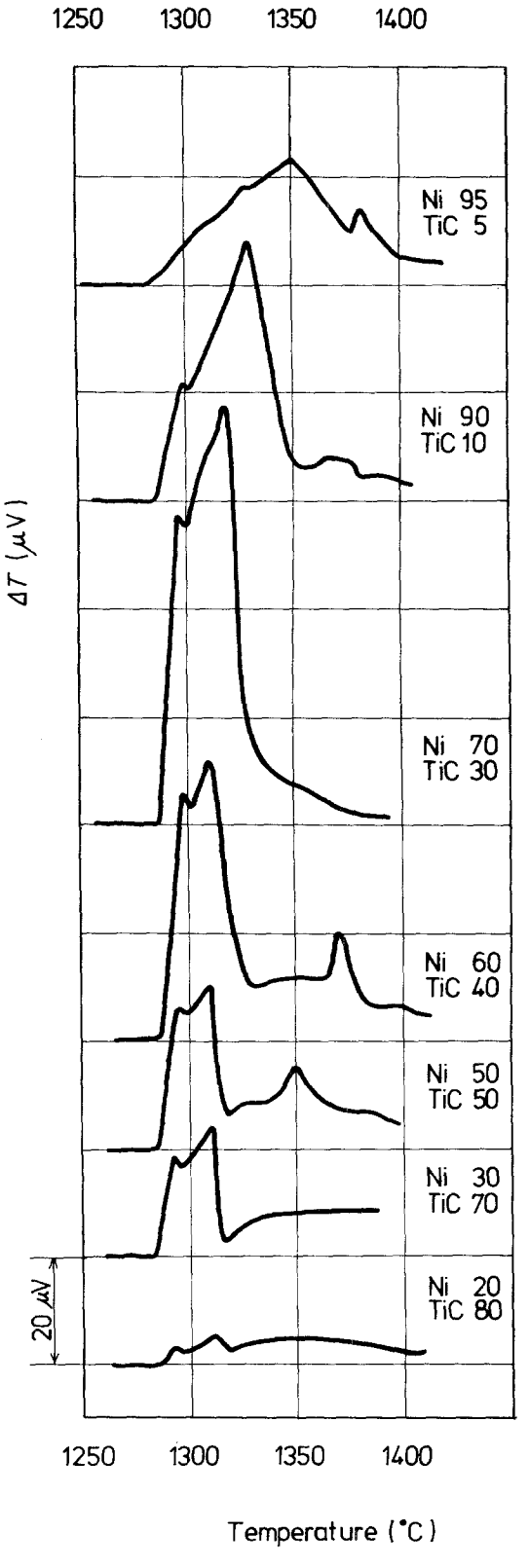


Figure 1 Differential thermal curves of the Ni–TiC system containing 5 to 90 wt % TiC.

3. Results and discussion

Fig. 1 shows the differential thermal curve of Ni–TiC system containing 5 to 90 wt % titanium carbide. Each specimen exhibited an endothermic reaction with three peaks in the curve. The Ni–30 wt % TiC specimen showed the sharpest reaction and the highest peak. The Ni–20 wt % TiC specimen exhibited a similar curve. The endothermic reaction initiation temperature at which the curves began to rise steeply, the temperature of the maximum peak and the differential thermal electromotive voltage of the maximum peak are summarized for each percentage of titanium carbide content in Table I. The first reaction began in the range 1284 to 1289° C.

All the specimens except the Ni–5 wt % TiC one initially showed peaks in the range 1290 to 1300° C, the second peaks, i.e. the maximum peaks, were in the range 1313 to 1329° C. It was noted that the maximum peak temperature tended to increase with decreasing titanium carbide content.

Fig. 2 shows the Ni–TiC pseudo-binary phase diagram of Stover and Wulff [3] for comparison. Comparing Fig. 1 with Fig. 2, it seems that there is a certain correspondence between the Ni–TiC pseudo-binary phase diagram and the differential thermal curve. For example, the first peak tem-

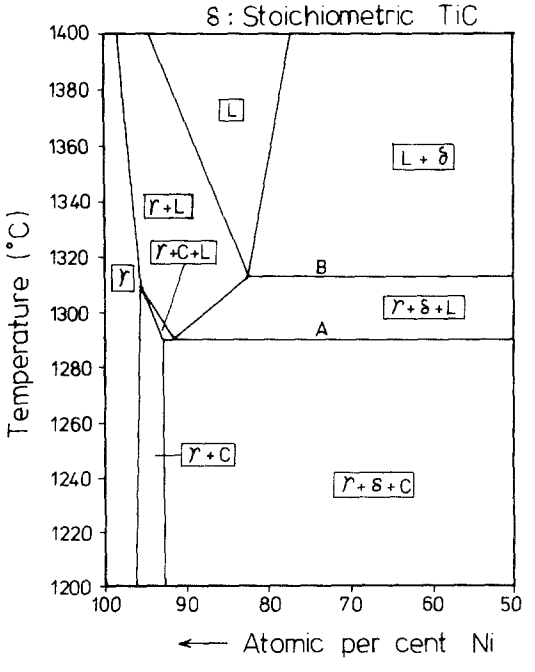


Figure 2 Ni–TiC pseudo-binary phase diagram of Stover and Wulff [3].

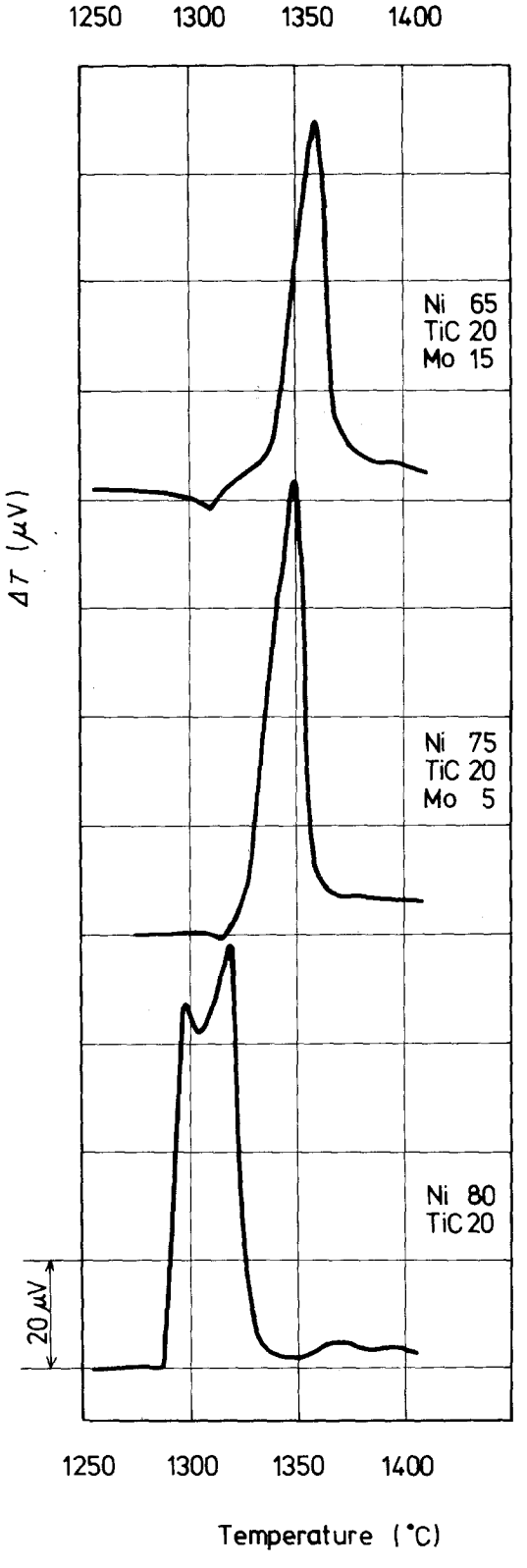


Figure 3 Differential thermal curves of the Ni–20 wt% TiC–Mo system containing 0, 5 and 15 wt% Mo.

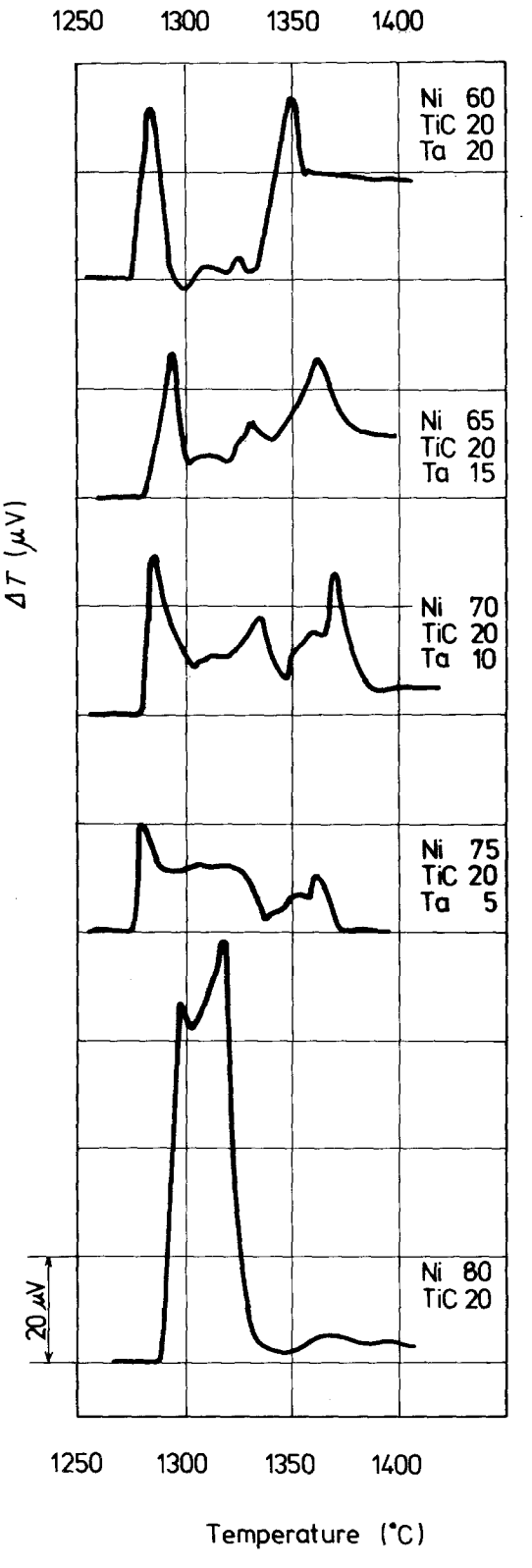


Figure 4 Differential thermal curves of the Ni–20 wt% TiC–Ta system containing 0, 5, 10 and 20 wt% Ta.

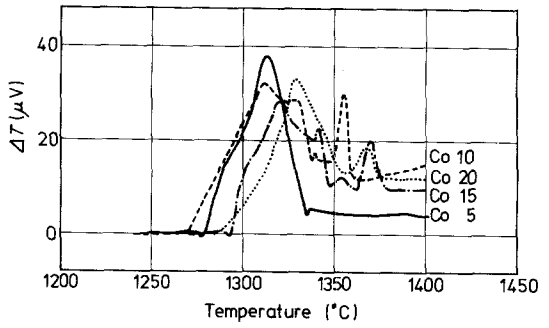


Figure 5 Differential thermal curves of the Ni–20 wt % TiC–Co system containing 0, 5, 15 and 20 wt % Co.

perature on the differential thermal curve corresponds to phase diagram A and the second peak temperature (maximum peak temperature) corresponds to phase diagram B. In these cases, the peak temperatures are slightly higher than the ones of A and B and this is considered to be due to a delay in measuring the differential thermal curve while heating at the certain rate.

Fig. 3 shows the differential thermal curves of the Ni–20 wt % TiC–Mo mixture containing 0, 5 and 15 wt % molybdenum. Every curve shows an endothermic reaction. It indicates that the reaction temperature increases as molybdenum is added. Table II shows the reaction initiation temperature, maximum peak temperature and thermal electromotive force with variation in Mo contents. The increase in reaction temperature on addition of Mo can also be seen by comparing Tables II and I.

Fig. 4 shows the differential thermal curves of the Ni–20 wt % TiC–Ta power mixture containing 0 to 20 wt % tantalum as well as the Ni–TiC–Mo mixture. They also show an endothermic reaction, however, the shapes of the curves are remarkably different. The reaction initiation temperature decreases with additon of Ta. These curves imply that the reactions take place over a wide range of temperature. The measurements are summarized in Table III.

Fig. 5 shows the differential thermal curves of the Ni–20 wt % TiC–Co mixture containing 0 to 20 wt % cobalt. They indicate that the curve at the beginning of the reaction is less steep than for the Ni–TiC system without Co. It is also found from Table IV that the reaction of the Co containing

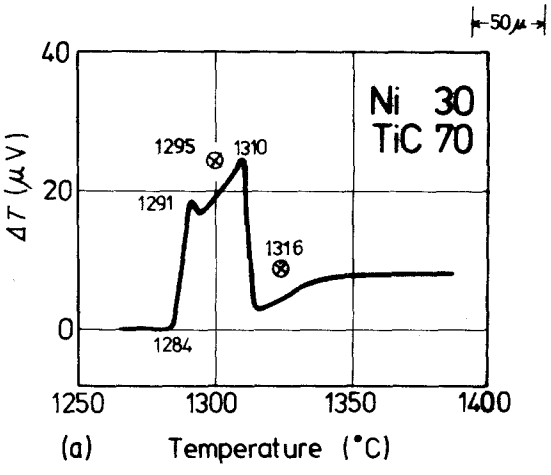
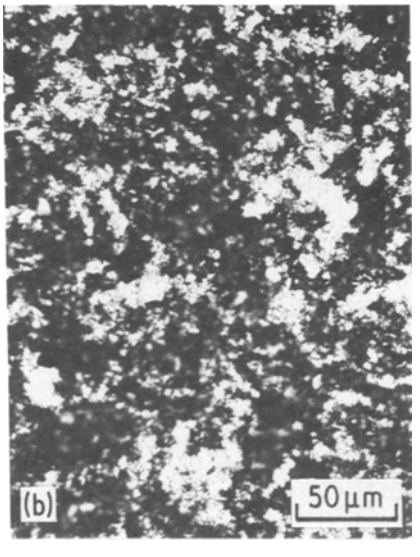
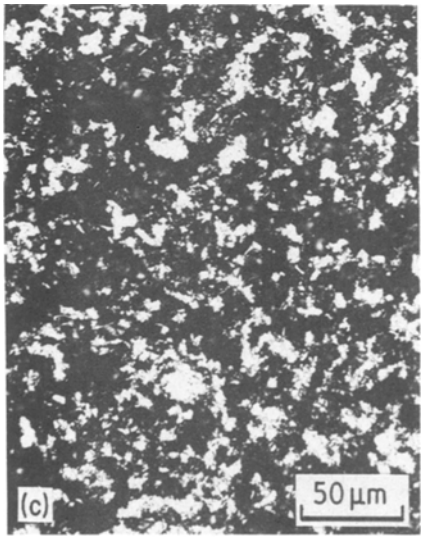


Figure 6 (a) Differential thermal curve of the Ni–70 wt % TiC system, (b) and (c) microstructures of the same system quenched from the temperature marked ⊗. (b) 1295° C and (c) 1316° C.





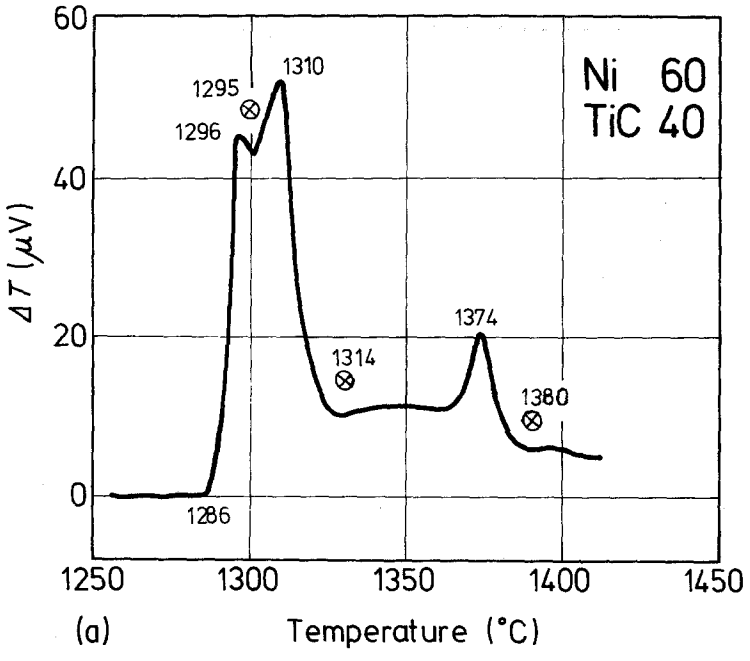


Figure 7 (a) Differential thermal curve of the Ni–40 wt % TiC system, (b), (c) and (d) microstructures of the same system quenched from the temperature marked ⊗. (b) 1295° C, (c) 1314° C and (d) 1380° C.

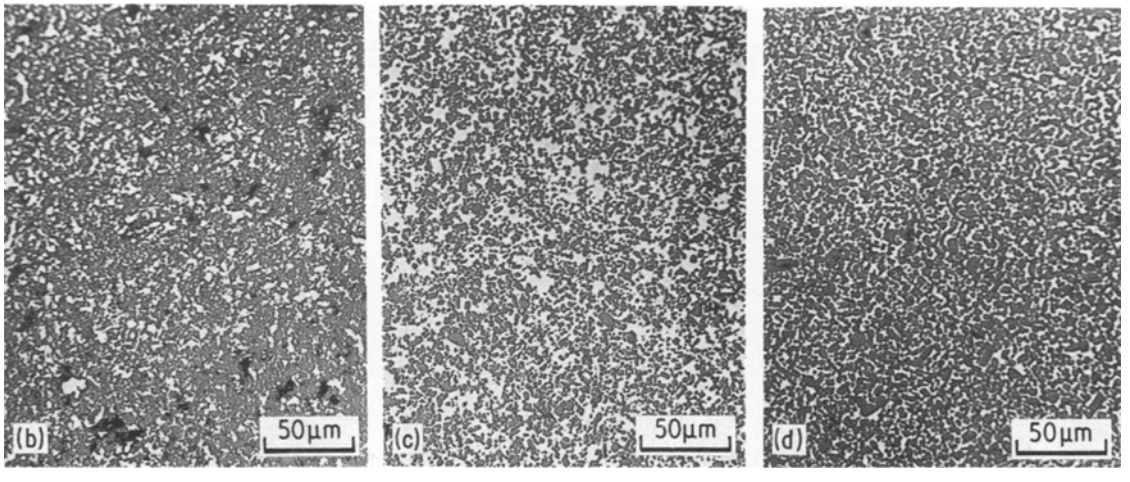
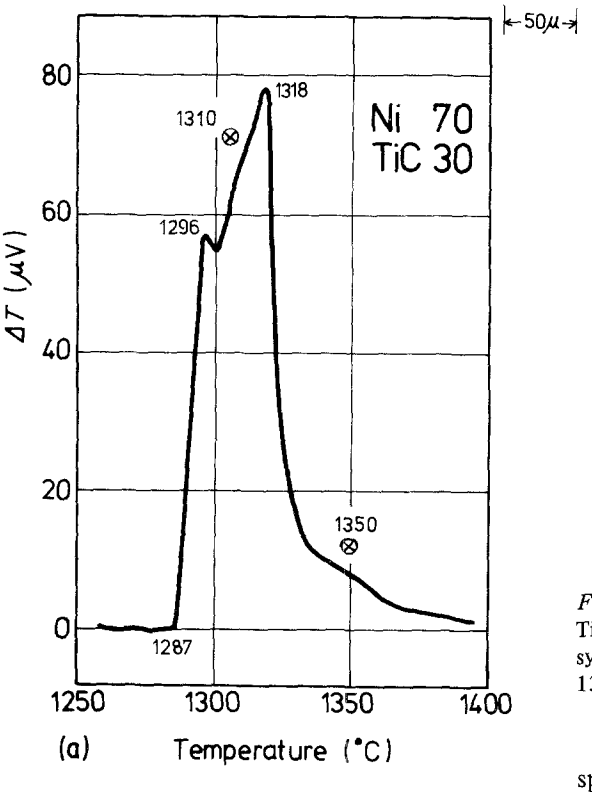


TABLE I Differential thermal analysis data of the Ni–TiC system

TiC content (%)	Endothermic reaction initiation temperature (° C)	Maximum peak temperature (° C)	Differential thermal electromotive voltage at maximum peak (μV)
5	1284	1350	24
10	1285	1329	49
20	1289	1318	78
30	1287	1318	78
40	1286	1310	51
50	1286	1310	30
60	1284	1312	26
70	1284	1310	23
80	1286	1310	7
90	1284	—	—



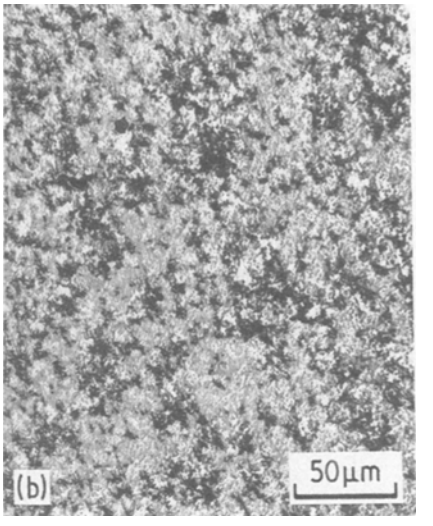
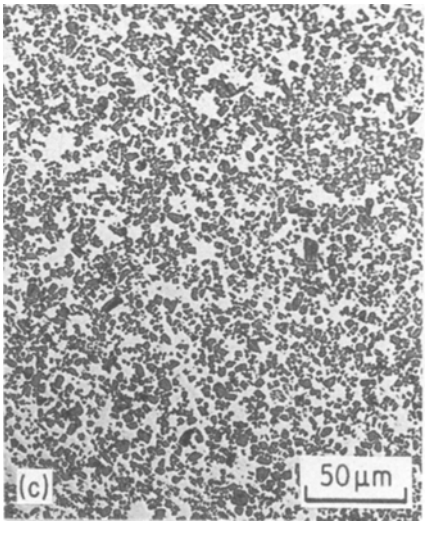


Figure 8 (a) Differential thermal curve of the Ni–30 wt % TiC system, (b) and (c) microstructures of the same system quenched from the temperature marked ⊗. (b) 1310° C and (c) 1350° C.



specimen is more moderate than the non-Co specimen.

Ni and TiC powders were blended in the same way as the specimen for differential thermal analysis, heated at a rate of about 3.5° C min^{-1}, then quenched from the temperature marked by the symbol ⊗ in Figs 6, 7 and 8. The results were observed by microphotography.

Fig. 6 shows the microstructure of the Ni–70 wt % TiC system quenched from 1295 and 1316° C. It was noted that the specimens quenched from 1316° C show finer structures than specimens quenched from 1295° C.

Fig. 7 shows the microstructures of the Ni–40 wt % TiC mixture quenched from 1295, 1314 and 1380° C. Many voids were observed in the specimen quenched from 1295° C, while few voids can be seen in the specimen quenched from

TABLE II Differential thermal analysis data of the Ni–TiC–Mo system

Content (%)			Endothermic reaction initiation temperature (° C)	Maximum peak temperature (° C)	Differential thermal electromotive voltage at maximum peak (μV)
Ni	TiC	Mo			
80	20	0	1289	1318	78
75	20	5	1315	1349	84
70	20	10	1312	1358	78
65	20	15	1311	1359	70
60	20	20	1302	1345	48

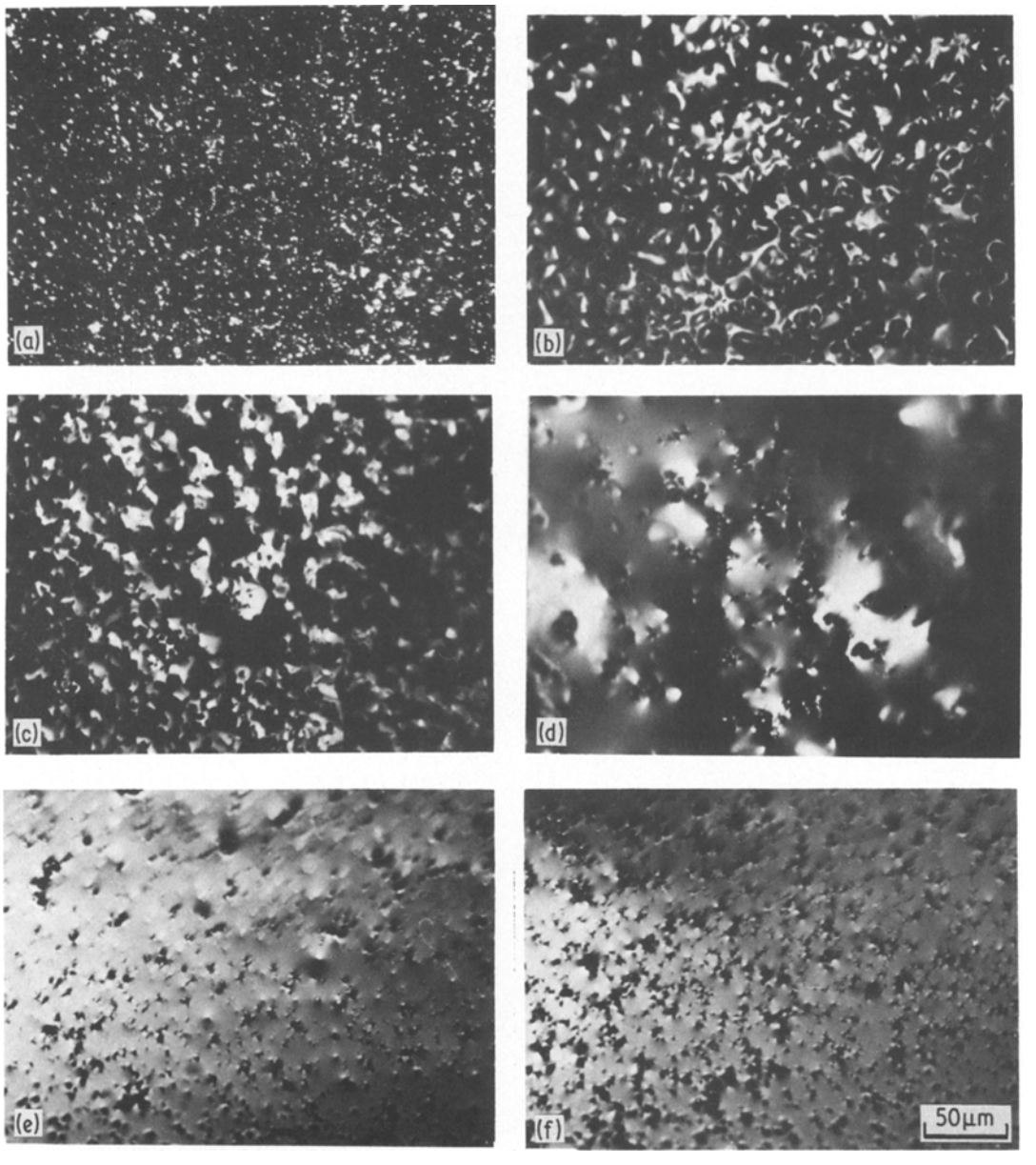


Figure 9 Microstructures of the Ni–30 wt % TiC system at high temperatures between 1000 and 1300° C. (a) 1000° C, (b) 1250° C, (c) 1300° C, (d) 1310° C, (e) 1320° C and (f) 1380° C.

TABLE III Differential thermal analysis data of the Ni–TiC–Ta system

Content (%)			Endothermic reaction initiation temperature (° C)	Maximum peak temperature (° C)	Differential thermal electromotive voltage at maximum peak (μV)
Ni	TiC	Ta			
80	20	0	1289	1318	78
75	20	5	1278	1281	21
70	20	10	1280	1285	30
65	20	15	1281	1294 1361	26
60	20	20	1276	1349	34

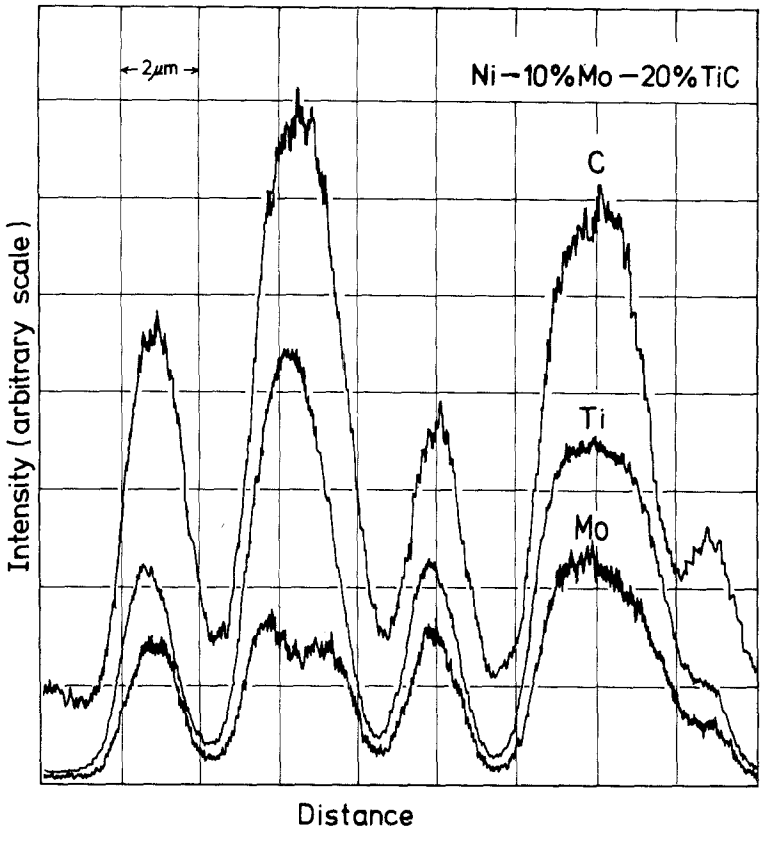


Figure 10 Scanning X-ray microanalyser curves for the melted Ni–20 wt % TiC–10 wt % Mo system.

1314° C. It also shows that TiC particles in the specimen quenched from 1380° C grow larger than in specimens quenched from 1314° C and the particles are dispersed uniformly.

Fig. 8 shows the microstructure of Ni–30 wt % TiC mixture quenched from 1310 and 1350° C. Agglomerated powders still remain in the specimen quenched from 1310° C, but a fine dispersion structure of TiC is observed in the specimen quenched from 1350° C.

Fig. 9 shows the microstructure of the Ni–30 wt% TiC mixture at high temperature which was prepared in the form of a disc by pressing powders under 2 ton cm^{-2} (196.31 MPa). These microstructure photographs were taken while taking the relationship with the differential thermal curve, shown in Fig. 8, into account.

From Fig. 9, which shows the specimen surface heated at a rate of 2° C min^{-1}, it is apparent that there is no change in the compressed powder state at 1000° C, but that the structure changes abruptly near 1250° C. The liquid phase partially appears at about 1265° C, more liquid phase appears at about 1300° C and then the whole of the observation surface is covered at 1310° C.

Areas of precipitation appear at about 1320° C and gradually increase on heating up to 1380° C (as shown in Fig. 9). It is also apparent from high

TABLE IV Differential thermal analysis data of the Ni–TiC–Co system

Content (%)			Endothermic reaction initiation temperature (° C)	Maximum peak temperature (° C)	Differential thermal electromotive voltage at maximum peak (μV)
Ni	TiC	Co			
80	20	0	1289	1318	78
75	20	5	1278	1312	38
70	20	10	1269	1312	32
65	20	15	1274	1321	29
60	20	20	1282	1329	33

temperature microscopic observations that the structure in the 1000 to 1300° C range is different from that in the 1310 to 1380° C range.

These differential thermal analysis results indicate that the Ni–TiC mixture with Mo, Ta and Co additions each show remarkable endothermic reactions with the appearance of a liquid phase which indicates the latent heat of fusion.

Assuming that the peak of the curve indicates the end of the reaction, differential thermal analysis must give useful information about sintering conditions for composite materials in the Ni–TiC system or similar systems.

It has been stated that the wettability between TiC and the matrix effects the dispersion of TiC [6] and the densification process in the preparation of the Ni–TiC alloy system [7]. Therefore, further studies will be required to understand the sintering process. However, from the measurement of wetting by the sessile drop method, the reaction which takes place at the surface of the TiC and the alloy, such as Ni–Mo, above 1300° C can not be considered negligible even for a short reaction time. Fig. 3 gives an example of the Ni–Mo–TiC system, which shows a sharp peak in the differential thermal analysis curve.

The scanning of the X-ray microanalyser for the Ni–20 wt % TiC–10 wt % Mo mixture at 1460° C indicates the movement of Mo to TiC as shown in Fig. 10. From the experimental results mentioned above, it is considered that the differential thermal analysis may give useful information about when the powder mixture is expected to react at high temperature.

4. Conclusions

Differential thermal analysis was performed for the Ni–TiC mixed powder system from room temperature to about 1400° C. It was found that the analy- gave useful information about sintering treatment.

In the Ni–TiC system, all the specimens showed an endothermic reaction starting at 1284 to 1289° C which reaction peaks above 1300° C. Moreover, the microstructure of Ni–30 wt % TiC changed in relation to the differential thermal analysis curve.

It was also apparent that the starting temperature and type of endothermic reaction changed remarkably on adding 5 to 20 wt % Mo, Ta and Co to each Ni–20 wt % TiC mixture.

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