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Melting Behaviour of (Ti, Mo)C–Ni and (Ti, W)C–Ni alloys

Dedicated to Prof. Dr.-Ing. habil. Dr.-Ing. E.h. W. Schatt on the occasion of his 75th birthday

The melting behaviour of alloys from Ni-rich portions of the quaternary systems Ni–Ti–Mo–C and Ni–Ti–W–C, where the monocarbide phases δ-(Ti, Mo)C and δ-(Ti, W)C coexist with metal melts, was investigated by means of differential thermal analysis (DTA), metallography, X-ray diffraction and SEM/EDS microanalysis. In a first approximation, the systems can be treated as pseudo-ternary with the components Ni–TiC–MoC and Ni–TiC–WC in the compositional range studied. Pseudo-ternary eutectic reactions: melt ⇔ $Ni_{(ss)}$ + δ-(Ti, Me)C + C (Me = Mo or W) have been observed and graphite can be in equilibrium with $Ni_{(ss)}$, δ-(Ti, Me) C and melt.

Schmelzverhalten von (Ti, Mo)C–Ni und (Ti, W)C–Ni-Legierungen

Das Schmelzverhalten von Legierungen der nickelreichen Bereiche der Systeme Ni–Ti–Mo–C und Ni–Ti–W–C in denen die Carbidphasen δ-(Ti, Mo)C bzw. δ-(Ti, W)C mit einer Metallschmelze koexistieren, wurde mittels Differential-Thermoanalyse, Metallographie, Röntgendiffraktometrie und energiedispersiver Mikroanalyse untersucht. In erster Näherung können diese Systeme als pseudoternär mit den Komponenten Ni–TiC–MoC bzw. Ni–TiC–WC betrachtet werden. Es wurden pseudoternäre eutektische Reaktionen Schmelze ⇔ $Ni_{(ss)}$ + δ-(Ti, Me) C + C (Me = Mo oder W) beobachtet. Graphit kann im Gleichgewicht mit $Ni_{(ss)}$, δ-(Ti, Me) C und Schmelze auftreten.

1 Introduction

The phase diagrams of the pertinent binary systems are well established. The ternary systems have also been investigated by various researchers. Rudy systematically studied the Ti–Mo–C and Ti–W–C systems in several isothermal sections and confirmed prior findings that Mo and W can replace Ti in δ-TiC to a large degree without changing the lattice structure of δ-TiC [1, 2].

Bäckerud et al. [3] investigated the melting behaviour of Ni–Ti–C alloys and reported that two ternary eutectics exist in the Ni-rich corner of the Ni–Ti–C system.

One eutectic reaction of melt ⇔ $Ni_{(ss)}$ + δ-TiC + C was observed at a composition of 7.4 at.% Ti, 80.3 at.% Ni and 12.3 at.% C at 1265 ± 5 °C (E1) and the other: melt ⇔ $Ni_{(ss)}$ + δ-TiC + Ni_3Ti at a composition of 16 at.% Ti, 80 at.% Ni and 4 at.% C and at 1295 ± 5 °C (E2). Stover and Wulff [4] have dealt with the phase equilibria in the Ni–Ti–C system in the temperature range from 870 °C to 1360 °C. According to their results, δ-TiC coexists with γ-(Ni, Ti, C) solid solution and with the other intermetallic compounds in the binary system Ti/Ni. The solid solubility of carbon in the intermetallic Ni–Ti compounds is negligible with exception of Ni_2Ti. If the data of Stover and Wulff [4] are compared to the results of Bäckerud et al., the ternary eutectic point E1 should rather be near to a composition of 6.6 at.% Ti and 10.7 at.% C. The position of the ternary eutectic point E1, reported by Bäckerud et al., appears to be too high in Ti and C. The composition of the solid solution of Ti + C in γ-Ni in equilibrium with TiC and C is approximately 2.6 at.% C and 3.5 at.% Ti at a temperature of 1260 °C.

The phase equilibria in the solid state in the system Ni–Mo–C have been investigated by Fraker et al. [5]. The melting behaviour of the Ni–Mo–C system in the Ni-rich region has been studied by Groschner et al. [6]. At least one ternary eutectic reaction: melt ⇔ $Ni_{(ss)}$ + Mo_2C + C has been observed at a composition of 70 at.% Ni, 18.5 at.% Mo and 11.5 at.% C and at 1250 ±5 °C. Between $Ni_{(ss)}$ and Mo_2C a pseudobinary eutectic appears to occur at a temperature of 1320 ± 20 °C and at an approximate composition of 70.5 at.% Ni, 19.5 at.% Mo and 10 at.% C. From this pseudobinary eutectic point, two melting troughs extend in two directions, one to the eutectic point with carbon of 1250 °C and the other toward a possible eutectic reaction between $Ni_{(ss)}$ and the η-carbides Ni_3Mo_3C + Ni_6Mo_6C. The two phase field where Mo_2C is coexistent with $Ni_{(ss)}$ is rather narrow with respect to the carbon content. At lower carbon contents, the η phases Ni_3Mo_3C and Ni_6Mo_6C coexist with $Ni_{(ss)}$ solid solution.

The melting behaviour of the Ni–W–C system has been experimentally investigated by Gabriel et al. [7] and Fiedler et al. [8] in the Ni-rich comer and a thermodynamic evaluation has been reported by Gustafson [9]. In this system, the phase equilibria between solid and liquid phases are characterised by a ternary peritectic point at 5.6 at.% W and 9.4 at.% C at 1344 °C comprising the reaction: melt + WC ⇔ $Ni_{(ss)}$ + C. The melting trough between WC and $Ni_{(ss)}$ intersects the connecting line between WC and Ni at about 1376 °C.

The melting behaviour of TiC-24 wt.% Mo-15 wt.% Ni alloys plus carbon additions corresponding to a [C]/([Ti]+[Mo]) atom ratio ranging from 0.8 to 1 was examined by Snell [10]. He indicated a temperature of incipient melting at 1285 °C for alloys with low carbon content and a temperature of incipient melting at 1265 °C for alloys with high carbon content. In both cases, (Ti, Mo) C is coexistent with $Ni_{(ss)}$ or a Ni-rich melt. Between these two extremes, the temperature of incipient melting was observed to be 1340 °C.

The system Ni–Ti–Mo–C has been investigated by Prima et al. [11]. They have observed a wide two phase field between the δ-(Ti, Mo) C_{1-x} and γ-$Ni_{(ss)}$ and postulated that this two phase field is bounded by the three phase equilibria $\delta + \gamma + Mo_2C$, $\delta + \gamma + \sigma$-(Mo, Ni) and $\delta + \gamma + Mo$ below 1380 °C. These findings are inconsistent with prior results by various other authors who have dealt with the ternary phase diagram Ni–Mo–C showing that MoNi does not coexist with $Ni_{(ss)}$ except at very low carbon contents and that Mo does not coexist with $Ni_{(ss)}$ at all. Hence, the phase diagram proposed by Prima et al. for the phase equilibria in the quaternary system Ni–Ti–Mo–C is probably correct with respect to the coexistence of the δ-(Ti, Mo) C phase with $Ni_{(ss)}$, but probably is erroneous with respect to the three phase fields and the quaternary four phase equilibria. Velikanova et al. [12] dealt with the quaternary Ni–Ti–Mo–C system as a pseudo-ternary system with the pseudo-components Ni–$TiC_{0.88}$–Mo and reported two invariant equilibrium points involving the participation of a liquid phase: melt + $Ni_{(ss)}$ ⇔ $Mo_{(ss)}$ + MoNi at 1250 °C and melt ⇔ $Mo_{(ss)}$ + MoNi + δ-TiC at 1220 °C, respectively. Their results, however, are probably not entirely correct and can not be used to construct the Ni–Ti–Mo–C system where δ-(Ti, Mo) C can coexist either with Ni_3Ti, Mo_2C or Mo_3Ni_3C.

Despite the technical interest for WC–Ni hardmetal alloys containing δ-TiC, only rather sketchy concepts do exist for the phase equilibria in the quaternary system Ni–Ti–W–C and no information at all for the melting behaviour. From microstructural observations in Ni bonded WC–TiC–Ni hardmetals, it is clear that δ-(Ti, W) C and WC do coexist with $Ni_{(ss)}$ in the solid state and that a (Ni, W, C) melt does coexist with the carbide phases WC and δ-(Ti, W) C. At low carbon contents, the appearance of η-carbide Ni_2W_4C has been observed in the microstructures. Hence, taking account of the well established two and three phase fields containing $Ni_{(ss)}$, it appears to be likely that a four phase field δ-(Ti, W) C + WC + Ni_2W_4C + $Ni_{(ss)}$ does exist.

Although the behaviour of W in the Ni–Ti–W–C system is expected to be similar to that of Mo in the Ni–Ti–Mo–C system, no systematic work has been performed so far. Moreover, no comprehensive and quantitative relationships have been determined between the melting behaviour of Ni in contact with δ-(Ti, Me) C_{1-x} (Me = Mo, W) containing different amount of Me contents, neither have phase equilibria and metallurgical reactions been established in the Ni–Ti–Me–C systems. The present investigation therefore aims to clarify some of the questions with respect to the metallurgical reactions during liquid phase sintering of hardmetals and cermet alloys.

Table 1. Alloy compositions and corresponding melting points in the Ti–Mo–C–Ni system.

Alloy	Ni	Ti	Mo	C	Eutectic intervals; °C		Starting materials
Number	at.%	at.%	at.%	at.%	ternary	binary	
T101	80.5	9.75	0	9.75	1266–1288	1294–1302	TiC, Ni
TM6105A	82.07	5.04	4.65	8.24	– 1292	1301–1331	$(Ti_{0.52}, Mo_{0.48}) C_{0.85}$, Ni
TM6104A	50.38	13.94	12.88	22.8	– 1307	1314–1343	
TM5106S	81.69	4.94	4.94	8.42	– 1294	1314–1342	$(Ti_{0.72}, Mo_{0.28}) C_{0.86}$, Mo_2C, C, Ni
TM5105S	81.69	4.94	4.94	8.42	1277–	1302–1332	$(Ti_{0.5}, Mo_{0.5}) C_{0.85}$, Ni
TM4106S	81.62	3.97	5.95	8.45	1270–1285	1304–1329	$(Ti_{0.72}, Mo_{0.28}) C_{0.86}$, Mo_2C, C, Ni
TM4105S	81.62	3.97	5.95	8.45	1276–1289	1304–1333	$(Ti_{0.4}, Mo_{0.6}) C_{0.85}$, Ni
TM9106	80.49	8.78	0.97	9.76	1265–1277	1292–1315	$(Ti_{0.72}, Mo_{0.28}) C_{0.86}$, Mo_2C, C, Ni
TM8106	80.55	7.77	1.95	9.72	1270–1284	1299–1315	
TM7106	80.47	6.84	2.93	9.77	1277–1292	1304–1323	
TM6106	81.09	5.89	3.47	9.56	1278–1292	1302–1318	
TM5106	80.52	4.87	4.87	9.74	1280–1295	1308–1326	TiC, Mo_2C, C, Ni
TM4106	80.51	3.9	5.85	9.75	1273–1292	1301–1315	
TM9105	80.5	8.78	0.98	9.75	1269–1279	1292–1315	(Ti_{1-x}, Mo_x) C, Ni x = 0.1, 0.2, 0.3, 0.5, and 0.6.
TM8105	80.78	7.69	1.92	9.61	1271–	1294–1320	
TM7105	80.51	6.82	2.92	9.75	1277–1286	1301–1322	
TM5105	80.52	4.87	4.87	9.74	1277–1290	1302–1324	
TM4105	80.51	3.9	5.85	9.75	1277–1289	1304–1327	
TM9104	48.42	23.21	2.58	25.79	1264–1266	1275–1293	
TM8104	48.34	20.66	5.17	25.83	1275–	1291–1316	
TM7104	48.36	18.07	7.75	25.82	1278–1292	1301–1314	
TMC1	60.96	2.02	16.93	20.09	1238–1264	(quaternary)	Ti, Mo, C, Ni
TMC2	60.97	2.08	17.08	19.87	1238–1264	(quaternary)	TiC, Mo_2C, C, Ni

2 Experimental Methods

In order to obtain a first insight into the metallurgical reactions which take place during liquid phase sintering of δ-(Ti, Me) C_{1-x} with nickel binder, several assumptions were made that were expected to facilitate the proper choice of compositions within the quaternary Ni–Ti–Me–C system. It was assumed that pseudobinary eutectic melting takes place between δ-(Ti, Me) C and Ni according to the phase reaction: δ-(Ti, Me) C + $Ni_{(ss)} \Leftrightarrow$ eutectic melt. The eutectic composition of the melt was anticipated to be in the vicinity of 89 mol% Ni and 11 mol% δ-(Ti, Me) C. The melting behaviour was measured for alloys with different Ti/Me ratios, with different carbon contents and with different carbide/nickel ratios. Furthermore, different starting materials, either pre-alloyed solid solutions δ-(Ti, Me) C or powder mixtures containing of TiC powder, Mo_2C (or WC) powder, carbon and Ni powder, were chosen.

Pre-alloyed ternary carbide powders were prepared by heating thoroughly mixed binary carbide powders with or without graphite, depending on the required products, at a temperature of 1900 °C for 4 to 12 hours under vacuum of 6 to 8×10^{-3} mbar. The pre-alloyed ternary carbide powders prepared in this way are very homogeneous as indicated by a clear splitting of the α_1/α_2 diffraction lines in the X-ray diffraction patterns.

The melting behaviour of carbide-metal powder mixtures was measured by differential thermal analysis (DTA). Recrystallized alumina crucibles were used and a platinum alloy was taken as a reference standard. The temperature was measured with a Pt/Pt-10% Rh thermocouple. The accuracy of the measurement was estimated to be ± 3 K as a result of calibration against various materials with known melting points such as Cu and Ni. DTA experiments were carried out repeatedly with the same alloy in an atmosphere of 800 mbar Ar at a heating and cooling rate of 10K/min. The maximum experimental temperature is about 1450 °C. At this temperature, all samples with the exception of samples TM9104, TM8104, TM7104 and TM6104A (see Table 1) were completely melted.

The microstructures of the DTA ingots were examined in an optical microscope. Quantitative analyses were performed by using a scanning electron microscope (JEOL JSM6400, Japan) equipped with an energy dispersive spectroscopy (EDS) detector. Phase identification was randomly checked by an X-Ray diffraction (XRD) method using Cu Kα radiation.

The starting powder materials used are given in Table 1 in the companion paper in this volume. Ni powder had a composition of > 99.7 wt.% Ni, < 0.1 wt.% O and < 0.1 wt.% C and was supplied by H. C. Starck, Germany.

3 Results

3.1 The (Ti, Mo) C–Ni Alloy System

DTA results are given in Table 1. Most alloys feature two peaks on their DTA plots. These peaks represent the pseudobinary eutectic reaction: melt $\Rightarrow Ni_{(ss)}$ + δ-(Ti, Mo) C and the pseudo-ternary eutectic reaction: melt $\Leftrightarrow Ni_{(ss)}$ + δ-(Ti, Mo) C + C, respectively. For alloys with substoichiometric carbon contents, such as TM5106S, TM6105A etc., only one DTA peak was observed, which was interpreted to indicate though that the compositions of the starting alloys correspond very closely to the pseudobinary eutectic points between Ni and δ-(Ti, Mo) C.

The alloy status of the starting materials has nearly no influence on the melting behaviour as shown in Fig. 1 and Fig. 2. With increasing Mo contents in the alloys, both, pseudobinary and pseudo-ternary eutectic temperatures, increase slowly by about 15 °C between TiC-Ni and ($Ti_{0.6}$, $Mo_{0.4}$) C–Ni and then tend to decrease again with higher Mo-content. Alloys with a high molar portion of carbides (~ 65 mol%), behave identically with respect to the melting behaviour compared to the alloys with pseudobinary eutectic composition.

In the microstructures of the ternary alloy T101 (Fig. 3), primary dendrites of Ni-solid solution, a binary eutectic constituent consisting of δ-TiC and $Ni_{(ss)}$ and a ternary eutectic constituent comprising δ-TiC, $Ni_{(ss)}$ and graphite (C) are visible. This observation agrees well with expectations and literature data. With substitution of Ti by Mo in the carbide phase the microstructures of the solidified quaternary alloy TM9106 feature similar microstructures as T101 (see Fig. 4).

The microstructures of the solidified alloys depend much more on the gross carbon content of the alloys than on the Mo content. Quaternary alloys with sufficient carbon con-

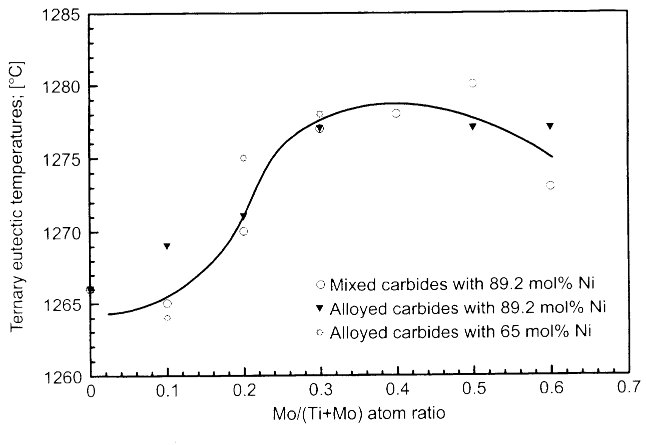

Fig. 1. Temperature of incipient melting of alloys with stoichiometric carbides in the (Ti, Mo) C–Ni system.

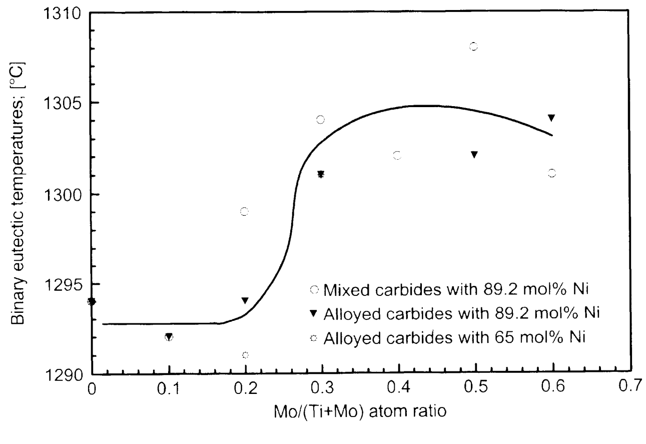

Fig. 2. Pseudobinary eutectic temperatures of alloys with stoichiometric carbides in the (Ti, Mo) C–Ni system.

tent (stoichiometry factor $z \approx 1$), irrespectively of their Mo content or whether they have been prepared from different starting materials, do show microstructures very similar to the alloy TM9106. However, alloys with a lower carbon content ($z = 0.85$), do not feature any ternary eutectic structure or only show traces of it (see Fig. 5 and Fig. 6).

The microstructures are consistent with the DTA results. The alloys with two peak characteristics on DTA plots (two eutectics) show both, binary and ternary eutectic microstructural features in the optical microscope. The Mo content of the starting carbides has nearly no influence on the microstructures, which is consistent with the fact that only minor effects of the [Mo]/([Ti] + [Mo]) ratio on the melting temperatures for alloys with 11 mol% (Ti_{1-x}, Mo_x) C ($x = 0$ to 0.6) have been observed. Alloys with low carbon contents (stoichiometry factor $z = 0.85$) develop no graphite precipitates in the microstructures or only very small amounts of graphite which is in agreement with the one-peak DTA plots (or two peaks which are very difficult to identify or to separate).

Although for alloys with high carbide contents (~65 mol%) the DTA curves indicate the occurrence of the eutectic reactions, actually no eutectic features have been observed in their microstructures. Instead, a "core-rim" structure within the hard phase can be observed. An example is given in Fig. 7. This phenomenon can be explained as follows. Even at high temperatures (~ 1400 °C), some carbides still remain undissolved in the melt. During cooling, the carbides dissolved in the melt reprecipitate around the undissolved carbides. Eutectic microstructures cannot be ob-

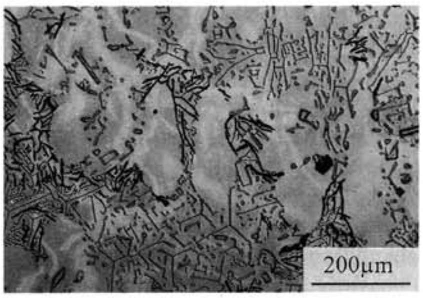

Fig. 3. Alloy T101, 10.8 mol% TiC–Ni. Primary Ni phase, binary eutectics and ternary eutectics with graphite.

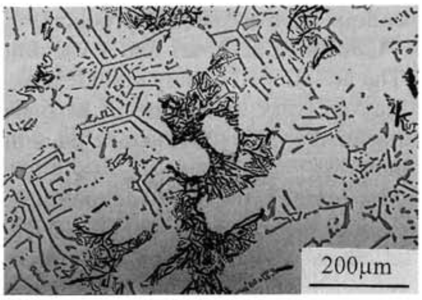

Fig. 4. Alloy TM9106, 10.8 mol% $(Ti_{0.9}, Mo_{0.1})$ C–Ni from mixtures of $(Ti_{0.72}, Mo_{0.28})$ $C_{0.86}$, Mo_2C, C and Ni. The microstructures are similar to that of T101.

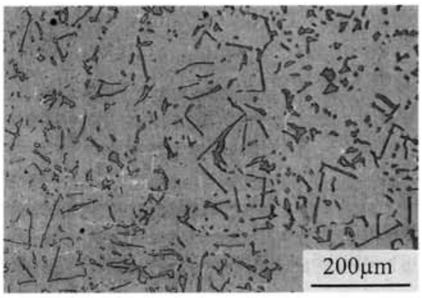

Fig. 5. Alloy TM5106S, 10.8 mol% $(Ti_{0.5}, Mo_{0.5})$ $C_{0.85}$–Ni from mixtures of $(Ti_{0.72},Mo_{0.28})$ $C_{0.86}$, Mo_2C, C and Ni. Primary Ni phase and pseudobinary eutectics without ternary eutectic microstructures.

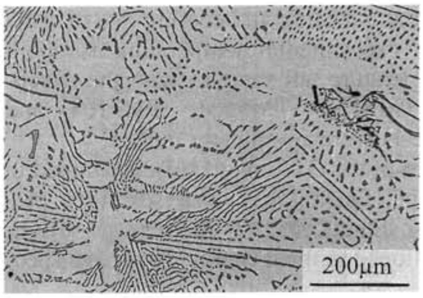

Fig. 6. Alloy TM5105S, 10.8 mol% $(Ti_{0.5},Mo_{0.5})$ $C_{0.85}$–Ni from mixtures of$(Ti_{0.5}, Mo_{0.5})$ $C_{0.85}$, and Ni. Primary Ni phase and binary eutectics with very few ternary eutectic areas.

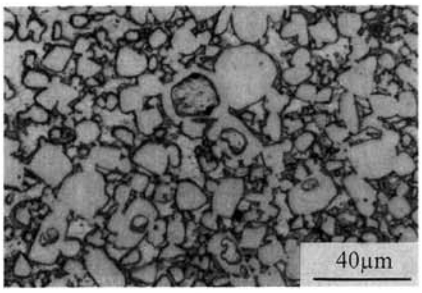

Fig. 7. Alloy TM8104, 65 mol% $(Ti_{0.8}, Mo_{0.2})$ C–Ni from powder mixtures of $(Ti_{0.8}, Mo_{0.2})$ C and Ni. Grey and white mixed carbides in Ni matrix without eutectics.

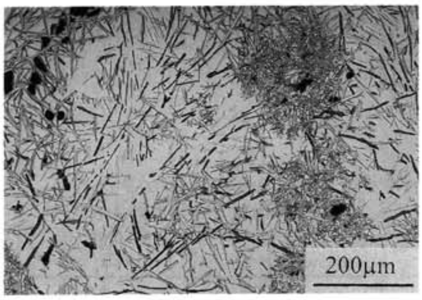

Fig. 8. Alloy TMC1, 25 mol% $(Ti_{0.1}$, Mo.9) $C_{1.05}$–Ni from powder mixtures of Ti, Mo, C and Ni.

Table 2. Alloy compositions and corresponding melting points in the Ti–W–C–Ni system.

Alloy Number	Ni at.%	Ti at.%	Mo at.%	C at.%	Eutectic intervals; °C ternary	Eutectic intervals; °C binary	Starting materials
T101	80.5	9.75	0	9.75	1266–1288	1294–1302	TiC, Ni
TW9106	80.48	8.79	0.98	9.76	1267–1281	1304–1336	TiC, WC, Ni
TW8106	80.52	7.79	1.95	9.74	1269–1281	1312–1348	
TW7106	80.51	6.82	2.92	9.75	1285–1300	1327–1356	
TW6106	80.50	5.85	3.90	9.75	1298–1312	1341–1362	
TW9105	80.51	8.77	0.97	9.74	1261–1279	1300–1331	(Ti_{1-x}, W_x) C, Ni x = 0.1, 0.2, 0.3, 0.4
TW8105	80.49	7.80	1.95	9.75	1265–1275	1304–1345	
TW7105	80.50	6.83	2.92	9.75	1273–1289	1317–1354	
TW6105	80.51	5.85	3.90	9.75	1293–1305	1331–1361	

served due to the preferential precipitation of the carbide around the nuclei.

The microstructures of alloys with a very high [Mo]/([Ti] + [Mo]) ratio, such as TMC1 and TMC2, are very different from those of the other alloys (see Fig. 8). Needle-like carbide precipitates can be observed together with a blocky graphite phase in a $Ni_{(ss)}$ matrix. This needle-like carbide phase has been identified as Mo_2C by XRD. The constituent with a very fine microstructure probably corresponds to a quaternary eutectic reaction comprising the phases: melt ⇔ $Ni_{(ss)}$ + δ-(Ti, Mo) C + Mo_2C + C at a comparatively low temperature of 1238 °C.

Quantitative SEM/EDS measurements indicate that the compositions of the pseudobinary eutectic microstructures do not vary significantly with respect to the carbide-nickel ratio. With increasing [Mo]/([Ti]+[Mo]) ratio of the starting materials (Ti_{1-x}, Mo_x) C from $x = 0$ to 0.6, the compositions of the pseudobinary eutectic microstructural constituents are nearly constant with respect to the carbide-nickel ratio and contain approximate 10.5 mol% δ-(Ti, Mo) C.

3.2 The (Ti, W) C–Ni Alloy System

In order to be able to compare with results arrived at in the Ni–Ti–Mo–C system, the alloys in the Ni–Ti–W–C system were chosen to have analogous compositions: 11 mol% (Ti_{1-x}, W_x) C and 89 mol% Ni. The starting carbides were either carbide mixtures of TiC and WC or pre-alloyed carbide solid solutions (Ti_{1-x}, W_x) C (x = 0, 0.1, 0.2, 0.3 and 0.4). The carbon contents correspond to the stoichiometric composition and hence the carbides should lie in the two-phase field of δ-(Ti, W) C and C in the Ti–W–C system.

DTA experiments show that the melting behaviour of alloys within the Ni–Ti–W–C system are similar to those of the Ni–Ti–Mo–C alloys as shown in Table 2. Two-peak characteristics on the DTA plots were observed, too. The metallurgical reactions can also be written schematically as follows and correspond to a pseudobinary eutectic reaction: melt ⇔ $Ni_{(ss)}$ + δ-(Ti, W) C and a pseudo-ternary eutectic reaction: melt ⇔ $Ni_{(ss)}$ + δ-(Ti, W) C + C.

The pseudobinary and pseudo-ternary eutectic temperatures of (Ti_{1-x}, W_x) C–Ni alloys, however, are significantly more dependent on the [Ti]/([Ti] + [W]) ratio in the carbides than the corresponding (Ti, Mo) C–Ni alloys. The pseudobinary and pseudo-ternary eutectic temperature of (Ti, W) C–Ni alloys increase from 1294 °C to 1341 °C and from 1266 °C to 1294 °C, respectively, with the [W]/([Ti] + [W]) atom ratio increasing from 0 to 0.4 (see Fig. 9 and Fig. 10). Furthermore, the alloying status of the starting materials also has strong influence on the eutectic temperatures of (Ti_{1-x}, W_x) C–Ni alloys. Alloys with carbide mixtures have higher pseudobinary and pseudo-ternary eutectic temperatures than those with pre-alloyed carbides of (Ti_{1-x}, W_x) C with x = 0 to 0.4.

The microstructures of alloys within the system (Ti, W) C–Ni are very similar to those of the (Ti, Mo) C–Ni alloys.

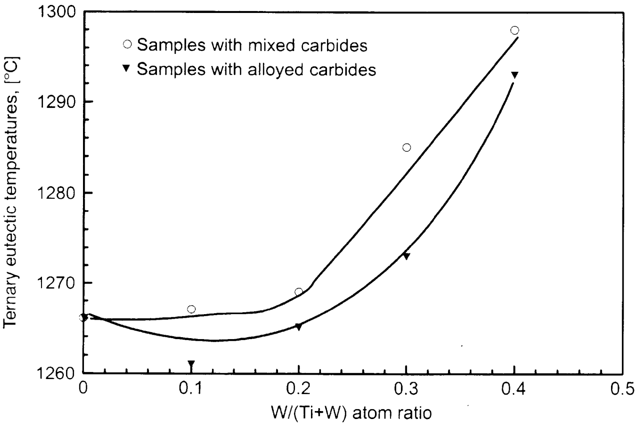

Fig. 9. Temperature of incipient melting of alloys with stoichiometric carbides in the (Ti, W) C–Ni system.

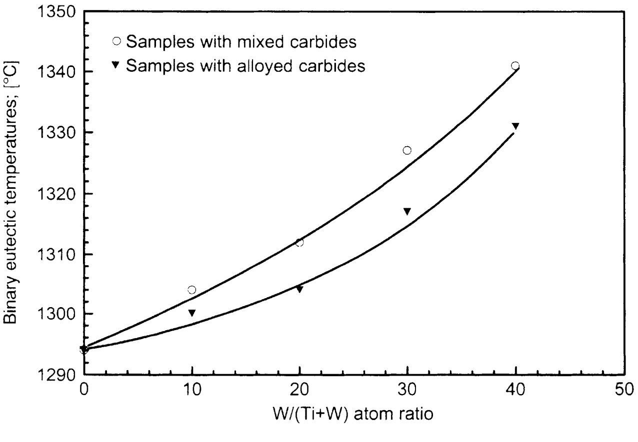

Fig. 10. Pseudobinary eutectic temperatures of alloys with stoichiometric carbides in the (Ti, W) C–Ni system.

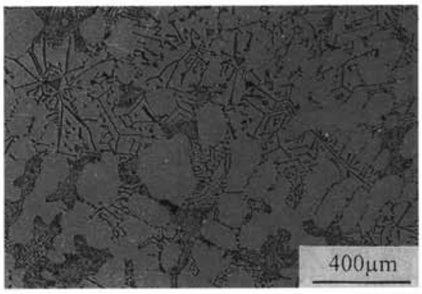

Fig. 11. Alloy TW9105, 10.8 mol% $(Ti_{0.9},W_{0.1})$ C–Ni. Primary Ni phase, Chinese script pseudobinary eutectics and ternary eutectics with graphite.

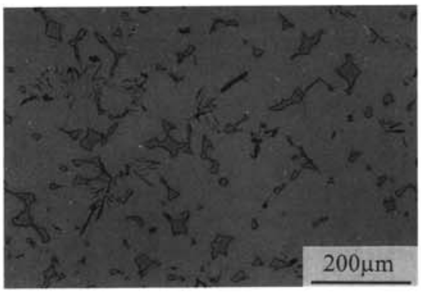

Fig. 12. Alloy TW6105, 10.8 mol% $(Ti_{0.6}, W_{0.4})$ C–Ni from mixtures of $(Ti_{0.6}, W_{0.4})$ C, and Ni. Graphite (C) lamellae and polygonal carbides exist in the Ni matrix.

Here, too, Ni primary phase, pseudobinary eutectic and pseudo-ternary eutectic constituents can be observed (see Fig. 11). The pseudo-ternary eutectic constituent contains graphite precipitates. No differences in microstructures between alloys with different starting materials but with the same gross composition have been observed. However, the "Chinese script" microstructural features which are characteristic for pseudobinary eutectic alloys in the system (Ti, Mo) C–Ni become less pronounced in the system (Ti, W) C–Ni, especially for alloys with high W contents. Instead of the "Chinese script" characteristics, polygonal bulk carbides are found in alloy TW6105 corresponding to $(Ti_{0.6}, W_{0,4})$ C–Ni as shown in Fig. 12.

4 Discussion

According to the results of the present work, the monocarbide phases δ-(Ti, Mo) C or δ-(Ti, W) C are coexistent with a Ni solid solution at lower temperatures and with a Ni melt containing substantial amounts of dissolved Ti, Mo (or W) and C at higher temperatures. Since the composition of the carbide with respect to carbon (stoichiometry factor) has not been varied to a great extent, no complex phases like Ni_3Mo_3C or Ni_6Mo_6C have been observed in the present investigation and need not be taken into consideration.

As seen in Fig. 13 and Fig. 14, the quaternary systems of Ni–Ti–Mo–C and Ni–Ti–W–C could, as a first approximation and in order to facilitate the visualisation, be treated as pseudo-ternary systems comprising the components TiC, "MoC" (or WC) and Ni. This treatment is of course not entirely correct, because in some experiments the phase graphite (C) is present and the phase $Ni_{(ss)}$, of course, has a four dimensional extension with respect to the dissolved elements Ti, Mo (or W) and C. Nevertheless, some of the more important experimental data can be graphically summarised under such an assumption and, in most cases, the melting behaviour of the systems will be analogous to the pseudobinary systems TiC–Ni.

Because of the very shallow slope of the melting trough of the pseudobinary eutectic section between δ-(Ti, Mo) C (or δ-(Ti, W) C), $Ni_{(ss)}$ and melt, the divariant behaviour of the pseudo-eutectic melting points is not perceptibly reflected in the DTA curves. Naturally, since the melt will generally have a composition that will deviate from the connecting line between the solid phases, the composition of the melt will gradually change upon solidification and eventually result in the solidification of a pseudo-ternary eutectic comprising the phases δ-(Ti, Mo) C (or δ-(Ti, W) C), $Ni_{(ss)}$ and graphite (C). The pseudo-ternary eutectic reactions give rise to a second peak in the DTA curve which, in most cases, will reflect the point of incipient melting of the alloy.

In the present study, the solidification behaviour of the quaternary systems shows analogy with the basic ternary system Ni–Ti–C. Ni–Ti–Me–C alloys (Me = Mo or

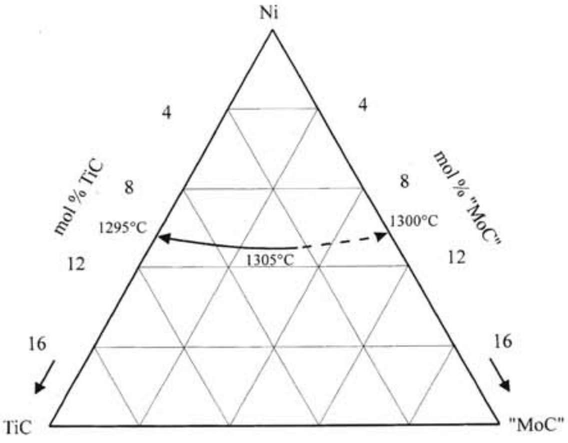

Fig. 13. Melting point behaviour of pseudo-ternary alloys Ni–TiC–MoC.

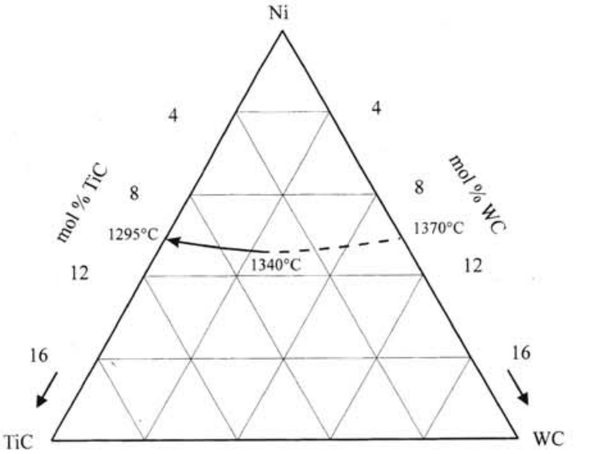

Fig. 14. Melting point behaviour of pseudo-ternary alloys Ni–TiC–WC.

W) with the chosen compositions start to solidify with the development of either primary $Ni_{(ss)}$ phase or mixed carbide phase δ-(Ti, Me) C, depending on the relative concentrations of the carbide in the alloys, then continues with the pseudobinary eutectic reaction: melt ⇔ $Ni_{(ss)}$ + δ-(Ti, Me) C and terminates with the pseudo-ternary eutectic reaction: melt ⇔ $Ni_{(ss)}$ + δ-(Ti, Me) C + C. In some cases, the solidification terminates already with the pseudobinary eutectic reaction if the carbon content C/(Ti+Mo) of the alloys is equal or lower than 0.85. However, intermetallic phases such as Ni_3Ti, NiMo or complex carbides like Ni_3Mo_3C have never been observed in the present investigation. Apparently, the carbon contents in the alloys have been sufficient to avoid the formation of low carbon phases such as complex carbides or intermetallic compounds.

Because of the very shallow slope of the pseudo-ternary melting trough comprising the phases: melt ⇔ $Ni_{(ss)}$ + δ-(Ti, Mo) C + C, and the non equilibrium conditions during the cooling cycle, the formation of a quaternary eutectic reaction that could and should be expected in the carbon and molybdenum rich portion of the Ni–Ti–Mo–C system: melt ⇔ $Ni_{(ss)}$ + δ-(Ti, Mo) C + Mo_2C + C can be observed only at rather high Mo/(Ti + Mo) atom ratios. In that case the composition of the δ-(Ti, Mo) C_{1-x} phase is set by the equilibrium with $Ni_{(ss)}$, C and Mo_2C. The quaternary eutectic temperature was measured to be 1238 °C. Probably the compositions of the experimental alloys TMC1 (or TMC2) come rather near to the quaternary eutectic composition.

5 Conclusion

As a first approximation, the phase equilibria and the melting behaviour in the studied range of the quaternary systems can be treated as pseudo-ternary with the components TiC, "MoC" (WC) and Ni. Graphite as a phase has been observed in equilibrium with $Ni_{(ss)}$, δ-(Ti, Mo) C and melt according to the pseudo-ternary eutectic reaction: melt ⇔ $Ni_{(ss)}$ + δ-(Ti, Me) C + C. Therefore, such a reaction does not agree with the pseudo-ternary formalism.

Because of the very large solubility of "MoC"and WC in δ-TiC, and within the compositional regions chosen, only mixed carbide phases δ-(Ti, Mo) C or δ-(Ti, W) C instead of pure "MoC" or WC phase have been observed together with $Ni_{(ss)}$ in the solidified alloys. The pseudobinary eutectic compositions of the systems (Ti, Mo) C–Ni and (Ti, W) C–Ni with respect to the molar ratio between carbide and metal do not change much with increasing Mo/(Ti + Mo) ratio and are similar to the TiC–Ni system. Mo additions do not greatly affect the eutectic temperatures, but W additions tend to increase them.

The solidification of (Ti, Mo) C_z–Ni alloys is controlled by the stoichiometry factor z. The solidification terminates with a pseudo-ternary eutectic reaction if 0.85 z 1 or with a pseudobinary eutectic reaction if 0.8 z 0.85. In the studied compositional range, neither the intermetallic phase Ni_3Ti nor the complex carbides of the type Ni_3Mo_3C or Ni_6Mo_6C have been observed.

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Literature

1. *Rudy, E.:* Compendium of Phase Diagram Data, Technical Report AFML-TR-65-2, Part V, May 1969.
2. *Rudy, E.:* J. Less-Common Met. *33* (1973) 245–273.
3. *Bäckerud, L.; Carlsson, B.; Oskarsson, R.; Mikus, M.:* Scand. J. Metall. *3* (1974) 225.
4. *Stover, E. R.; Wulff, J.:* Trans. AIME *215* (1959) 127.
5. *Fraker, A. C.; Stadelmaier, H. H.:* Trans. Met. Soc. AIME *245* (1969) 847.
6. *Groschner, M.; Ettmayer, P.; Lengauer, W.; Kolaska, H.:* La Revue de Metallurgie-CIT/Science et Genie des Materiaux (1994) 1767.
7. *Gabriel, A.; Pastor, H.; Deo, D. M.; Basu, S.; Allibert, C. M.:* Intern. J. Refract. & Hard Met. *5* (1986) 215.
8. *Fiedler, M. L.; Stadelmaier, H. H.:* Z. Metallkd. *66* (1975) 402.
9. *Gustafson, P.; Gabriel, A.; Ansara, I.:* TRITA-MAC-0263, Royal Institute of Technology, Stockholm, Sweden (1985).
10. *Snell, P. O.:* Planseeber. Pulvermetall. *22* (1974) 91.
11. *Prima, S. B.; Velikanova, T. Y.; Shepoval, T. A.:* Diagr. Systoyaniya Tugophavk System, Kiev (1980) 48–71 (in Russian).
12. *Velikanova, T. Y.; Petrenko, L. A.; Shabanova, S. V.:* Poroshk. Metall. *1* (1979) 37.

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