*Journal of Thermal Analysis and Calorimetry, Vol. 80 (2005) 599–606*

# PRESSURE EFFECT ON THE PHASE TRANSITIONS IN Ni-BASE MULTICOMPONENT SYSTEMS

*A. G. Padalko*[1*], *A. N. Veselov*[1], *S. P. Avduhin*[2], *G. D. Nipan*[3] *and V. P. Sanygin*[3]

[1]RAS Institute of Physical Chemistry of Ceramics, 48 Ozernaya, 119361 Moscow, Russia
[2]NPO 'Saturn' 13 Kasatkina, 129301 Moscow, Russia
[3]RAS Institute of General and Inorganic Chemistry, 31 Leniskii pr., 117907 Moscow, Russia

The phase transformations in the three Ni-base alloys at the temperature range up to 1500°C and at the pressure of 170 MPa were studied. Solidus, γ'-phase dissolution/precipitation, carbides dissolution/precipitation and liquidus temperatures are established. Multiple exceeding of the Ni-base alloys characteristic temperatures pressure coefficients over metal components ones (up to 10 times) is observed both at the heating and cooling scans during the experiments on the differential barothermal analysis. On the DBA curves had been obtained at 170 MPa, there are from two to three peaks, which connected with the carbides dissolution/precipitation, while on the each conventional DTA curve there was merely one 'carbide' thermal effect. The liquidus temperature pressure coefficients correlate with the Ni melting point pressure coefficient.

***Keywords:*** *carbides, characteristic temperatures, differential barothermal analysis (DBA), γ+γ' eutectics, γ'-phase, Ni-base alloys*

## Introduction

Dynamic and forward development of all of the science and technology fields determines appearance of new materials, which have new properties; in that number have the improved ability of resistance to various physical and chemical factors. Development of progressive materials, independently of their belonging to metals, semiconductors, ceramics, glass, polymers, composites etc., is based on construction of the 'property-composition' diagrams [1, 2]. The leading role in such study carrying out, without any doubt, belongs to thermal analysis, which combines the differential thermal analysis (DTA), differential scanning calorimetry, and other techniques [3]. Thanks to its simplicity and high importance of the results, in the number of thermal analysis techniques the differential thermal analysis occupies the leading role. By using the DTA data most of the both inorganic and organic binary and ternary systems are studied. It should be noted, the DTA technique successfully uses not only for the phase equilibriums study at atmospheric and lower, but at the high, up to 10 GPa, pressure. Phase equilibriums at high pressure study have not only the pure scientific interest, which allows establishing the nature of the phenomena occurs, for instance, in the Earth's core. Large importance has the phase transitions temperatures at high pressure knowledge for the materials science. The last circumstance is connected with the high pressure – high temperature techniques for the purpose of advance materials producing. The static barothermal effect (hot isostatic pressing) finds the new and new fields of application for producing of high density inorganic materials with the sharply improved mechanical, electrical and other properties.

To the number of such materials belong the heat-proof Ni-base alloys, the base for engine parts, which operates at extremely high thermal and mechanical loads. At existing diversity of the developed alloys, and significant quantity of chemical elements in their composition, the list of their main structure (phase) components consists of four names. In their number are γ-solid solution based on Ni (1), γ'-phase based on $Ni_3Al$ (2), non-equilibrium eutectics γ+γ' (3), carbides and borides $M_xC_y$ and $M_xB_y$, respectively (4).

Among mentioned above Ni-base alloys phase components the γ'-particles plays the especial role. It connected with the high (up to 70 vol%) content of γ'-phase in the alloys, and its determinative value at mechanical properties formation. In according with the existing conceptions, the physical chemistry nature of the γ'-particle strengthening is, from one hand, the chemical and structure similarity of γ-solid solution and γ'-particles, and from another hand the difference of the lattice constant of these two components. The last circumstance leads to local mechanical strengths, enhances the mechanical properties of Ni-base alloys.

In the optimized nickel alloy the γ'-phase particles should have the strict cubic geometry with the rib size of 0.45 μm. Despite of dendrite nature of the solidification, which determines the difference of the γ'-phase elimination conditions in the axes and interdendrite

---

[*] Author for correspondence: padalko@orc.ru

*1388–6150/$20.00*

*Akadémiai Kiadó, Budapest, Hungary*
*Springer, Dordrecht, The Netherlands*

spaces, the geometry identity should be in the all alloy's volume. In some cases in the γ -solid solution layers between elemental γ'-cubes it is necessary γ'-nanoparticles with the dimensions of 10 to 30 nm presence.

Non-equilibrium γ+γ' eutectic inclusions are the structure component of many nickel alloys. Their appearance is connected with the real, essential non-equilibrium conditions of the alloys solidification. Concentration of such inclusions in the nickel alloys after solidification not exceed of 2–3 vol%, however these inclusions plays the significant role in the mechanical properties formation, because of γ+γ' globules are the places of mechanical strengths concentration. Taking into account this circumstance, the content of such inclusions should be minimized.

Carbide $M_xC_y$ and boride $M_xB_y$ particles, which form on eutectic mechanism, enhances the alloys resistance to mechanical strengths. However their useful properties becomes in an entire measure in the case, when carbides chemical composition, size and morphology are close to optimum. For the non-metallic inclusions the polyhedral morphology of minimal surface is preferable, which allows to escape of the enhanced mechanical strengths concentration in the system 'hard particle-soft matrix'.

In such a way, in Ni-base alloys γ'-particles, eutectics γ+γ' and non-metallic carbides and borides inclusions forms the complex heterogeneous system in the nickel solid solution (γ -solid solution). To optimize the quantitative and qualitative characteristics of γ -matrix, γ', γ+γ' and non-metallic particles, one can use the nickel alloys thermal processing. In some cases, the thermal treatment durability reaches tens of hours. During the treatment the alloy homogenization takes place. At thermal processing γ' and non-metallic particles occurs morphologic alterations, which allows to improve appreciably the nickel alloys mechanical properties.

It is clear, that most significant results of thermal treatment using can be achieved at the accurate knowledge of the characteristic temperatures of Ni-base alloys, as follows: the solidus, liquidus, dissolution/precipitation of the γ', γ+γ' and non-metallic particles. One of the main techniques of these temperatures searching is the differential thermal analysis. Because of the thermal treatment at high pressure wide using for the various materials [4, 5], first of all to the density rising, the question is appear, is it rightfully to use the characteristic temperatures data of Ni-base alloys, obtained at $P \leq 0.1$ MPa, to the processes, occurs at barothermal treatment at hydrostatic pressure of inert gas, compressed up to 200 MPa. In other words, it seems there is determined necessity on the phase transitions on Ni-base alloys study at high pressure. To get the information is possible by differential barothermal analysis (DBA) using [6].

## Experimental

Experiments at high pressure one carry out in the hot isostatic pressing plant 'Abra', where one can place the differential thermal analysis cell. To provide the necessary level of pressures and linear temperature varying one can use the hot isostatic pressing plant possibilities, but the DBA curves recording one can carry out by the additional electronic blocks and PC (Fig. 1) with the corresponding software. More detailed the differential barothermal analysis technique is described in the previous paper [6].

As the initial materials one can choose three nickel alloys with the various chemical compositions (Table 1), which are determined the various characteristic temperatures sets.

The samples had the different structure (#1 alloy had the single crystal structure, #2 and #3 alloys had the equal-axes structure). The mass of the samples one can vary in the wide limits from of 500 up to 10 000 mg. To the large mass samples one can use the graphite cell, allows to carry out the thermal measurements at samples dimensions of 10 mm of diameter and height up to 30 mm. Such using of the various measure cells and samples dimensions one can apply to the technique optimization and sensitivity rising. To the #1 alloy one can use also the samples of the special shape, allowed their placing immediately on the ceramics protected differential thermocouple. In the last case it was impossible to melt the samples; however the technique sensitivity was rose.

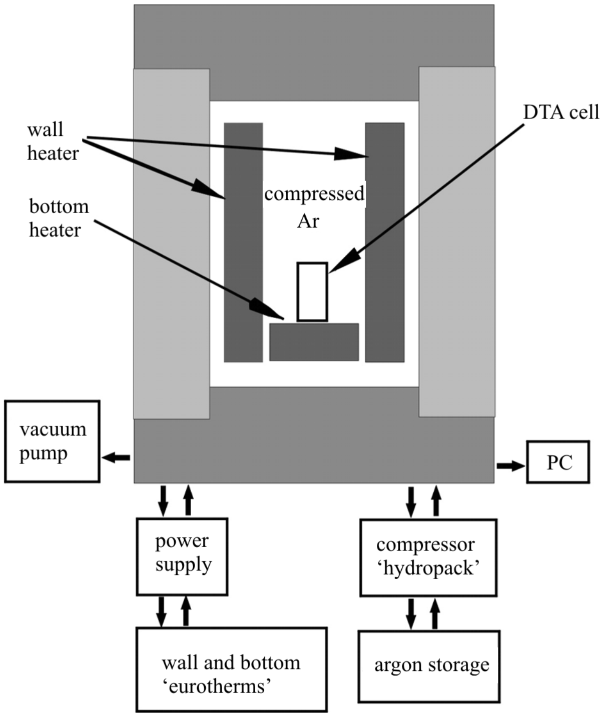

**Fig. 1** Block-scheme of differential barothermal analysis

**Table 1** Chemical composition of the DBA-studied Ni-base alloys

| Alloy | Elements/mass% | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Cr | Ti | Mo | W | Re | Ta | Al | Co | Nb | B | Zr | C |
| #1 | 5.0 | 0 | 1.0 | 8.3 | 4.0 | 4.0 | 6.0 | 9.0 | 1.5 | 0.015 | 0.05 | 0.15 |
| #2 | 9.0 | 2.6 | 1.5 | 10.3 | 0 | 0 | 3.4 | 9.8 | 1.1 | 0.03 | 0 | 0.18 |
| #3 | 14.8 | 3.7 | 0.5 | 6.7 | 0 | 0 | 4.0 | 8.8 | 0 | 0.01 | 0 | 0.10 |

The characteristic temperatures determination was carried out at two, three or four of heating/cooling cycles. Obtained data had been averaged and such data one can use to calculating of the characteristic temperatures pressure coefficients, which determines as

$$\frac{\mathrm{d}T_\mathrm{i}}{\mathrm{d}P}=\frac{T_\mathrm{iP}-T_\mathrm{ic}}{P}\,[\mathrm{K\ MPa^{-1}}]$$

where $\mathrm{d}T_\mathrm{i}/\mathrm{d}P$ – the characteristic temperature pressure coefficient, $T_\mathrm{iP}$ – the value of characteristic temperature at high pressure, $T_\mathrm{ic}$ – the value of characteristic temperature at conventional conditions, $P$ – the pressure (equal to 170 MPa).

At the experimental DBA curves processing one can take into account, that all the alloys have the intervals of solidification, and the γ↔γ+γ’ phase transformation takes place in the solid-state, but the precipitation/dissolution of the $M_xC_y$ carbides occurs in the temperature range of $T_S \leq T \leq T_L$, that is in the liquid–solid material state.

## Results and discussion

All the obtained DBA curves had the complex shape, which reflects the phase transformations, occurs at heating/cooling of the studied multicomponent nickel alloys. At high pressure the phase transformations consequence is the same as the transitions has been observed at the conventional ($P \leq 0.1$ MPa) conditions.

As it mentioned above, at the chemical elements quantity, which reaches of 12–15, in the nickel alloys composition, the main phase components amount is equal to four, as follows; 1) Ni-base solid solution Ni<Co, Cr, Mo, W …> (γ-solid solution); 2) $Ni_3Al$-based solid solution $Ni_3Al$<Co, Cr, Mo, W…> (γ’-phase); 3) none-equilibrium eutectics γ+γ’; 4) carbides $M_xC_y$ and borides $M_xB_y$.

It should be noted, the globular γ+γ’ inclusions can appear in the nickel alloys volume either as a result of non-equilibrium solidification nature, or at probable deviations from the alloys chemical composition.

On the DBA curves obtained the thermal effects, connected with all mentioned phase components, were established. At the large amount of the thermal effects it is advisable to analyze the DBA curves consequently on each nickel alloys component.

### *Heating scans*

### γ+γ’ eutectics

The thermal effect of the eutectics melting/crystallization in the Ni alloys has the minimal value because of total amount of this phase component is not exceed of 2 mass%. However, on the DBA curves of all three studied alloys the γ+γ↔*L* phase transitions were established.

To the #1 alloy with the highest solidus and liquidus temperatures the start of eutectics melting one can observe (Figs 2a, b) at 1327°C. This transition at conventional conditions occurs at 1313°C. In such a way, the melting temperature pressure coefficient of γ+γ’ eutectics had value of 0.08 K $\mathrm{MPa^{-1}}$. In the #2 alloy at 170 MPa the temperature of the eutectics melting beginning (Fig. 2c) had the value of 1240°C on the curve of heating. At conventional conditions of thermal scanning the γ+γ’↔*L* transition occurs at 1242°C, and, therefore, the pressure coefficient value is close to zero. The temperature of γ+γ’ eutectics melting in the #3 alloy at heating and 170 MPa had the value of 1293°C (Fig. 2d). On the conventional curves the corresponding peak is absent. Therefore the pressure coefficient had not been determined.

### γ’-phase temperature of full dissolution

γ’-phase Ni<Cr, Co, Mo, W …> in the multicomponent nickel alloys have been formed as a result of γ-solid solution spinodal dissociation in the solid-state at the alloy cooling. γ-solid solution and γ’-phase have the same crystal lattices [8]. The difference among them concludes in the crystal structure. γ-solid solution is the disordered solid solution of substitution, with the lattice parameters, insignificantly differs from ordered γ’-phase crystal lattice. Such closeness of the lattice parameters, despite of significant γ-phase concentration in the alloys, which have been reached of 70 vol%, determines the small thermal effect at this transformation both at heating and cooling scans.

The end of γ’-phase dissolution process at heating in #1 alloy at 170 MPa (Figs 2a, b) occurs at 1301°C, that significantly higher, than at alloy heating at conventional DTA. The temperature difference $T_{\gamma'}^{170}-T_{\gamma'}^{0.1}=$ 28°C, that leads to value of $\mathrm{d}T_{\gamma'}(1)/\mathrm{d}P=0.16\ \mathrm{K\ MPa^{-1}}$. In the #2 alloy (Fig. 2c) with the solidus temperature

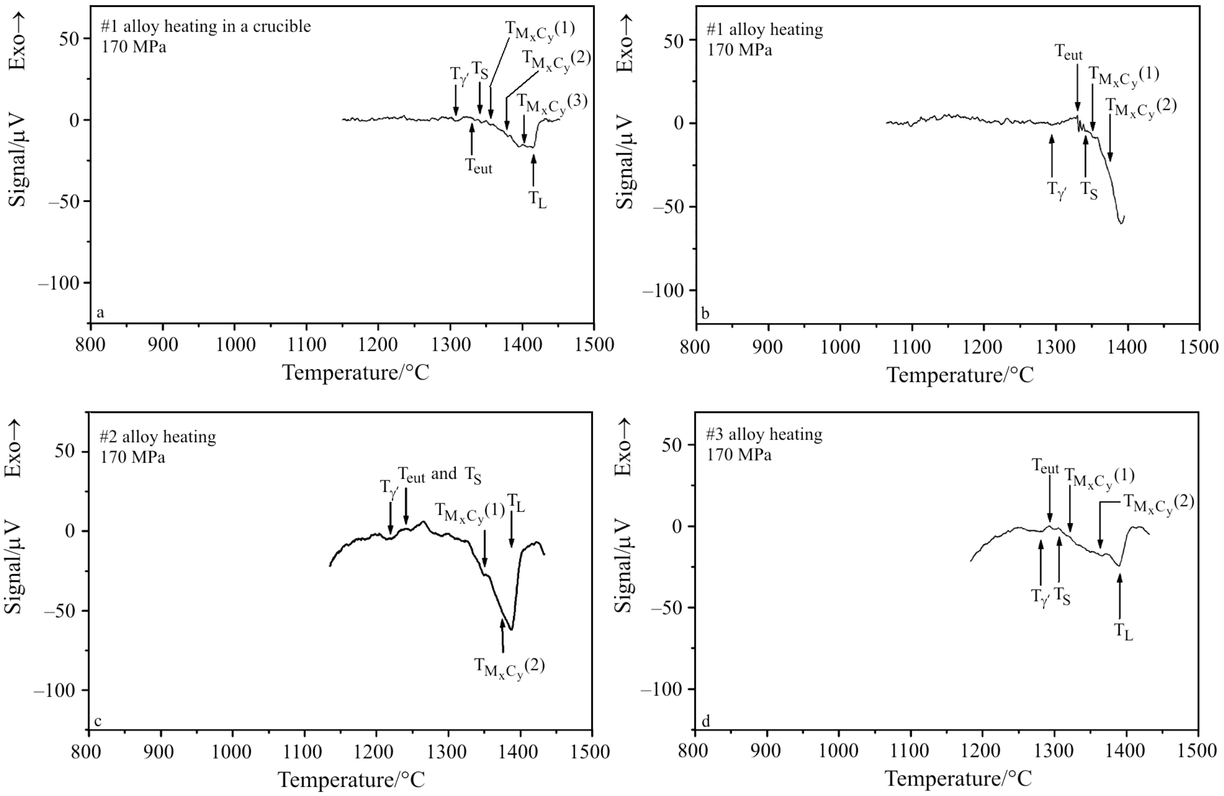

**Fig. 2** Typical DBA heating curves of Ni-base alloys: a – #1 alloy, placed in the crucible, b – #1 alloy, placed immediately on the thermocouple, c – #2 alloy, d – #3 alloy

of 1242°C the temperature of full dissolution rising was noted, and at $\Delta T_{\gamma'}$ =13°C the pressure coefficient had value of $\mathrm{d}T_{\gamma'}(2) / \mathrm{d}P = 0.08$ K MPa$^{-1}$. In the #3 alloy at 170 MPa (Fig. 2d) γ'-phase full dissolution one can observe at 1281°C. The same transformation at atmospheric pressure occurs at 1192°C, that gives the significant difference $\Delta T_{\gamma'}(3)$ =89°C, which leads to pressure coefficient of $\mathrm{d}T_{\gamma'}(3) / \mathrm{d}P$ =0.52 K MPa$^{-1}$.

## Temperature of solidus

Temperature of solidus at 170 MPa for #1 alloy (Figs 2a, b) had the value of 1327°C. The same transformation at conventional conditions occurs at 1313°C, and corresponding pressure coefficient has the value 0.08 K MPa$^{-1}$. In the #2 alloy (Fig. 2c) $T_S$ is practically unaltered, but in #3 alloy (Fig. 2d) the value of $\mathrm{d}T_S(3)/\mathrm{d}P$ was more significant, up to 0.05 K MPa$^{-1}$.

## Carbides

In the #1 alloy on the DBA curves of heating (Figs 2a, b) at analysis of four curves, one of which had been obtained on standard technique with the sample placing in the alumina crucible (Fig. 2a), but three DBA curves were recorded in the 'half-melting' mode, with the sample placing immediately on the ceramics protected thermocouple (Fig. 2b). On these data at the process of heating the carbides $M_xC_y$ dissolution at three temperatures of 1355 ($M_xC_y(1)$), 1378 ($M_xC_y(2)$) and 1403°C ($M_xC_y(3)$) occurs. It should be noted, that on the conventional DTA data, there are no thermal effects, connected with the carbides dissolution. On this reason the pressure coefficients one can not determine. In the #2 alloy on the DBA curves of heating one can observe two types of carbides at 1346 and 1377°C, while on the conventional DTA curves such peaks were absent. In this case the pressure coefficients one can not determine, too. In the third alloy, similar to the two previous ones, one can observe dissolution of two types of carbides $T_{\mathrm{MxCy}}(1)$ and $T_{\mathrm{MxCy}}(2)$ at 1321 and 1362°C, accordingly. To the first carbides type the pressure coefficient is insignificant, and is equal –0.04 K MPa$^{-1}$. For the second carbide on the cause mentioned above, the pressure coefficient did not establishe.

## Temperature of liquidus

The liquidus temperature on all of the DBA curves, except the case of non-crucible samples placing, were recorded most clear (Figs 2, 3). In the #1 alloy the liquidus temperature was established at 1415°C, but at conventional conditions this value was at 1390°C,

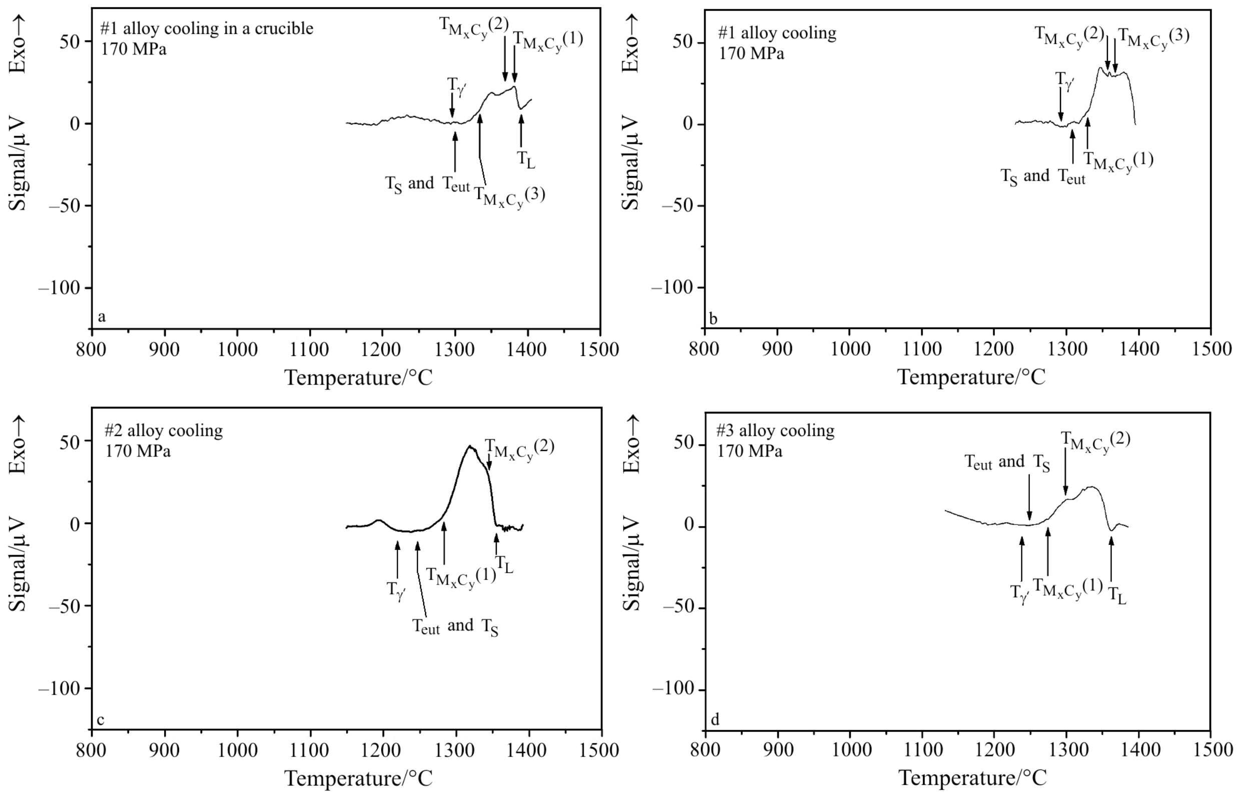

**Fig. 3** Typical DBA cooling curves of Ni-base alloys: a – #1 alloy, placed in the crucible, b – #1 alloy, placed immediately on the thermocouple, c – #2 alloy, d – #3 alloy

and the pressure coefficient had the value of $dT_L(1)/dP=0.14$ K MPa$^{-1}$. In the #2 alloy the liquidus temperatures difference at 170 and 0.1 MPa has reached of 37°C, and the pressure coefficient has the maximum for the studied alloys value of $dT_L(2)/dP=0.22$ K MPa$^{-1}$. In the #3 alloy the temperature difference was $\Delta T(3)=35$°C, and the pressure coefficient had value of $dT_L(3)/dP=0.2$ K MPa$^{-1}$.

## *Cooling scans*

### γ+γ’ eutectics

At the cooling of the #1 alloy (Figs 3a, b) the temperature of eutectics crystallization process end was equal to 1305°C. In according to the data on phase transitions in the alloy at conventional conditions, the temperatures of eutectics melting and solidus are coincide, were equal to 1253°C, and pressure coefficient had the value of 0.3 K MPa$^{-1}$. On the cooling DBA curve of the #2 alloy (Fig. 3c), the end of transformation had the value of 1255°C. Observed difference between eutectics melting temperatures should be connecting with unnecessary accuracy at analyzing of this transformation because of the high level of electric noise. Pressure coefficient of this transformation to #2 alloy had the value of 0.25 K MPa$^{-1}$. On the DBA and DTA curves of #3 alloy cooling (Fig. 3d) at 170 and 0.1 MPa the temperatures of the crystallization end had the values of 1242 and 1248°C, accordingly, and the pressure coefficient had the value of 0.04 K MPa$^{-1}$.

### γ’-phase

At cooling of the nickel alloys, heated up to 1500°C, after process of solidification, γ-solid solution, which is in the solid-state, dissociates on γ and γ’-phases mixture. The transformation beginning in the #1 alloy (Figs 3a, b) occurs at 1295°C. From the data on conventional DTA, the transformation $\gamma+\gamma'\leftrightarrow L$ beginning occurs at 1253°C. In such a way, the pressure coefficient is $dT_{\gamma'}(1)\,/\,dP=0.25$ K MPa$^{-1}$. On the cooling curves the pressure coefficient of the #2 alloy (Fig. 3c) had the value 0.05 K MPa$^{-1}$. At #3 alloy cooling the pressure coefficient is $dT_{\gamma'}(3)\,/\,dP=0.25$ K MPa$^{-1}$, which is twice less than the value had been obtained at heating.

### Temperature of solidus

For the #1 alloy solidus temperature at 170 MPa had value of 1305°C, but at conventional conditions one can determine $T_S=1253$°C, that leads to the pressure coefficient $dT_S(1)/dP=0.30$ K MPa$^{-1}$. The solidus temperature of the #2 alloy (Fig. 3c) on DBA curves of cooling at 170 MPa had the value of 1255°C. Corresponding temperature difference $T_S^{170}(2) - T_S^{0.1}(2) = 43°C$, which determines the value of $dT_S(2)/dP = 0.25$ K MPa$^{-1}$. The solidus temperature of the #3 alloy did not dependent practically on applied pressure (Fig. 3d), therefore small value of $dT_S(3)/dP = 0.04$ K MPa$^{-1}$ has been obtained.

### Carbides

At #1 alloy cooling on the DBA curves one can observe three carbides types precipitation, similar to the heating scan, at the temperatures of 1378 ($T_{MxCy}(1)$), 1362 ($T_{MxCy}(2)$), and 1331°C ($T_{MxCy}(3)$). On the conventional DBA curves the corresponding effects were absent, and the pressure coefficients were not established. At #2 and #3 alloys solidification at 170 MPa one can admit precipitation of two carbides types, also, in contrast to the one carbide, which observes on the conventional DTA curves.

### Temperature of liquidus

At the cooling mode the solidification beginning occurs with the less supercooling degree, than at the conventional conditions, and the pressure coefficients had the values of 0, 0.15 and 0.09 K MPa$^{-1}$ to the alloys of 1, 2 and 3 numbers.

The data have been obtained in the paper, are generalized in the Tables 2 and 3.

At analyzing of the data obtained, it should be noted, that small alterations of the solidus temperatures at heating mode are connected with the small alteration of the alloys specific volume, occurs in the melting process of the multicomponent alloy. Transiting into liquid state first, most fusible portions of the alloy components, such as the globules of the $\gamma+\gamma'$ eutectics, so insignificantly alters the alloy specific volume that the solidus temperature alteration do not observe practically. This circumstance, independently whether the specific volume increases or decreases at heating over solidus temperature, is the reason of the solidus temperature small alteration.

Significant difference of the DBA and DTA curves had been obtained at the pressure of 170 and 0.1 MPa concludes in the thermal effects presence on the high pressure curves, connected with the dissolution/precipitation of the $M_xC_y$ carbides. To explaining this phenomenon, it should be considered the known data on the carbides in the heat-proof nickel alloys [7]. On contemporary ideas, it is possible three types of carbides formation in the Ni-base alloys, as follows: monocarbides MC, carbides $M_{23}C_6$ and $M_6C$ (*M* – metal) (Table 4).

The chemical formulas of the most probable carbides are determined by the alloy chemical composition, particularly by carbon, strong (Ta, Hf, Nb, Ti, etc.) and weak (Cr, W, Mo) carbides-formative elements. Thermodynamically most stable are the monocarbides MC. The carbides stability decreases in the line of $HfC_{0.94}$ (non-stoichiometric) ($T_m$=3960°C), TaC ($T_m$=3445°C), NbC ($T_m$=3390°C), HfC (stoichiometric) ($T_m$=3190°C), WC ($T_m$=2780°C), MoC ($T_m$=2700°C) [8].

In the composition of the nickel alloys' carbides W and Mo takes part, also, and in the less quantities Ni and Cr, with the atoms substitution in the metal sub-lat-

**Table 2** Data on the phase transitions in the Ni-base alloys at 170 MPa on the peaks and half-peaks of heating

| Special temperatures | Average value at 170 MPa/°C | Data at 0.1 MPa/°C | Pressure coefficients $dT_i/dP$/K MPa$^{-1}$ |
|---|---|---|---|
| #1 Ni-base alloy at 170 MPa on the four peaks | | | |
| $T_{\gamma'}$ | 1301 | 1273 | 0.16 |
| $T_{eut}$ | 1327 | 1313 | 0.08 |
| $T_S$ | 1327 | 1313 | 0.08 |
| $T_{M_xC_y}(1)$ | 1355 | no peak | – |
| $T_{M_xC_y}(2)$ | 1378 | no peak | – |
| $T_{M_xC_y}(3)$ | 1403 | no peak | – |
| $T_L$ | 1415 | 1390 | 0.14 |
| #2 Ni-base alloy at 170 MPa on the three peaks | | | |
| $T_{\gamma'}$ | 1221 | 1207 | 0.08 |
| $T_{eut}$ | 1240 | 1242 | ~0 |
| $T_S$ | 1240 | 1242 | ~0 |
| $T_{M_xC_y}(1)$ | 1346 | no peak | – |
| $T_{M_xC_y}(2)$ | 1377 | no peak | – |
| $T_L$ | 1387 | 1350 | 0.22 |
| #3 Ni-base alloy at 170 MPa on the two peaks | | | |
| $T_{\gamma'}$ | 1281 | 1192 | 0.52 |
| $T_{eut}$ | 1293 | – | – |
| $T_S$ | 1300 | 1291 | 0.05 |
| $T_{M_xC_y}(1)$ | 1321 | 1328 | –0.04 |
| $T_{M_xC_y}(2)$ | 1362 | no peak | – |
| $T_L$ | 1390 | 1355 | 0.20 |

**Table 3** Data on phase transitions in the Ni-base alloys at 170 MPa on the peaks and half-peaks of cooling

| Special temperatures | Average value at 170 MPa/°C | Data at 0.1 MPa/°C | Pressure coefficients $dT_i/dP$/K MPa$^{-1}$ |
|---|---|---|---|
| #1 Ni-base alloy at 170 MPa on the four peaks | | | |
| $T_{\gamma'}$ | 1295 | 1253 | 0.25 |
| $T_{eut}$ | 1305 | 1253 | 0.30 |
| $T_S$ | 1305 | 1253 | 0.30 |
| $T_{M_xC_y}$ (1) | 1331 | no peak | – |
| $T_{M_xC_y}$ (2) | 1362 | no peak | – |
| $T_{M_xC_y}$ (3) | 1378 | no peak | – |
| $T_L$ | 1390 | 1395 | ~0 |
| #2 Ni-base alloy at 170 MPa on the three peaks | | | |
| $T_{\gamma'}$ | 1227 | 1212 | 0.05 |
| $T_{eut}$ | 1255 | 1212 | 0.25 |
| $T_S$ | 1255 | 1212 | 0.25 |
| $T_{M_xC_y}$ (1) | 1284 | no peak | – |
| $T_{M_xC_y}$ (2) | 1342 | 1342 | 0 |
| $T_L$ | 1363 | 1350 | 0.08 |
| #3 Ni-base alloy at 170 MPa on the two peaks | | | |
| $T_{\gamma'}$ | 1234 | 1192 | 0.25 |
| $T_{eut}$ | 1242 | 1248 | –0.04 |
| $T_S$ | 1242 | 1248 | –0.04 |
| $T_{M_xC_y}$ (1) | 1298 | 1297 | ~0 |
| $T_{M_xC_y}$ (2) | 1274 | no peak | – |
| $T_L$ | 1362 | 1346 | 0.09 |

**Table 4** Ni-base alloys carbides components

| No. | Carbide | Quasi-chemical reactions of the carbides formation | Thermal stability/°C | Conditions of carbides formation |
|---|---|---|---|---|
| 1 | MC | $L=\gamma+$MC | 1300 | at alloy solidification |
| 2 | $M_{23}C_6$ | MC+$\gamma$=$M_{23}C_6$+$\gamma$' | 1050 | at low-temperature ageing |
| 3 | $M_6C$ | MC+$\gamma$=$M_6C$+$\gamma$' | 1250 | at alloy solidification |

tice of carbides. MC carbides have been formed from the melt at the eutectic temperature on the reaction $L\leftrightarrow\gamma$+MC, and such carbides are stable up to 1300°C. Medium and high content of Cr in the alloy leads to the $M_{23}C_6$ carbides formation. Such carbides forms in the solid-state, and the thermal effects appearance, connected with their dissolution/precipitation, is hardly probable. $M_6C$ carbide can form in the alloy with W high content on the reaction MC+$\gamma\leftrightarrow M_6C$+$\gamma$'. Its precipitation can take place at solidification also, and this carbide is stable up to 1250°C at chemical composition varying from $W_6C$ to $Ni_3W_3C$.

From the Table 4 it follows, that in the cast heat-proof alloy after solidification should exist two probable carbides, namely MC and $M_6C$, which have been formed at the alloy solidification in the temperature range of $T_S<T<T_L$, and have close ranges of existence.

Third peak appearance on the #1 alloy DBA curves, which connects with carbides dissolution/precipitation, does not exclude appearance of the 'high pressure' carbide phase for this alloy, which can have a composition, did not describe in literature.

The alloys liquidus temperature rising correlates with the relative solidus temperature of $T_{m\ Ni}/T_{S\ i}$ (where $T_{m\,Ni}$ – Ni melting point at 0.1 MPa, $T_{S\,i}$ – #*i* alloy solidus temperature at 0.1 MPa). This is shown in Fig. 4, were performed the dependence of the liquidus

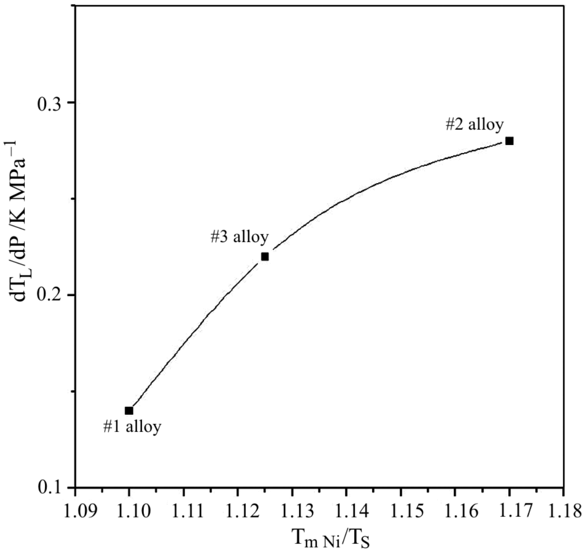

**Fig. 4** Correlation between liquidus temperatures pressure coefficients and nickel melting point

temperature pressure coefficients of the studied alloys as a function of the relative solidus temperature $dT_L(i)/dP=f(T_{m\ Ni}/T_{S\ i})$. In according with Fig. 4, the pressure coefficient $dT_L/dP$ is decreased approaching to the Ni (alloy base) melting point. Taking it into account, it is possible to suppose, that Ni-base alloys, which have the highest liquidus temperatures, will have lowest liquidus temperature pressure coefficient, and coincides with the Ni melting point pressure coefficient, equal to 0.03 K $MPa^{-1}$ [9].

## Conclusions

The phase transformations of three Ni-base alloys at the temperature range up to 1500°C and at pressure of 170 MPa were studied. Pressure coefficients of solidus, γ'-phase dissolution/precipitation, carbides dissolution/precipitation and liquidus temperatures are established. The obtained Ni-base alloys characteristic temperatures pressure coefficients showed their large value comparing with the melting points pressure coefficients of the pure metal components of the alloys. Multiple exceeding of the Ni-base alloys characteristic temperatures pressure coefficients over metals melting points ones (up to 10 times) is observed both at the heating and cooling scans during the experiments on the differential barothermal analysis. On the DBA curves had been obtained at 170 MPa, there are from two to three peaks, which connected with the carbides dissolution/precipitation, while on the conventional DTA curves was recorded merely one ‘carbide’ thermal effect. The liquidus temperature pressure coefficients correlate with the Ni melting point pressure coefficient.

## Acknowledgements

The work is supported by Russian Foundation for Basic Research, grants 02-03-32918, 05-03-32533.

## References

1. V. Ja. Anosov and S. A. Pogodin, Main Fundamentals of Physicochemical Analysis, Moscow–Leningrad, Academy of Sciences of USSR 1947 (in Russian).
2. V. Ja. Anosov, M. I. Ozerova and U. Ja. Fialkov, Fundamentals of Physicochemical Analysis, Moscow, Nauka 1976 (in Russian).
3. J. Šesták, Thermophysical Properties of Solids, Academia Prague 1984.
4. J. Westerlund and A. Vimercati, MPR, February 2000.
5. A. S. Helle, K. E. Easterling and M. F. Ashby, Acta Metall., 33 (1985) 2163.
6. A. G. Padalko, A. N. Veselov, S. P. Avduhin, G. D. Nipan and V. P. Sanygin, J. Therm. Anal. Cal., 72 (2003) 791.
7. R. E. Shalin, I. L. Svetlov, E. B. Kachanov, V. N. Toloraia and O. S. Gavrilin, Single Crystals of Ni-base Heat-Proof Alloys, Moscow, Mashinostroenie 1997 (in Russian).
8. Chemical Encyclopedic Vocabulary, Moscow, Sovetskaia Encyclopedia 1983 (in Russian).
9. E. U. Tonkov, Compounds Phase Transformations at High Pressure, Handbook, Moscow, Metallurgiya 1988 (in Russian).