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Effect of repeated remelting on the chemical composition and structure of nickel alloys

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Abstract

The results of preliminary tests and studies on the effect of repeated remelting of selected nickel alloys on changes in the chemical composition and structure were presented. The aim was to investigate possible management and utilisation of post-production waste (rejects, parts of the gating system, etc.). It has been reported that repeated remelting of IN-713C alloy had no significant effect on changes in its chemical composition. Only aluminium slightly reduced its content due to melting loss, as confirmed further by the results of ATD thermal analysis. On the other hand, in MAR-247 alloy after remelting, a decrease in the content of Cr, Ta, Hf, and C in particular, was observed. To re-use the post-production waste, it is necessary to make up the content of some elements (especially trace elements) and carry out the modification process.

Keywords: nickel superalloys, remelting, macrostructure, modification, columnar and equiaxial grains, ATD thermal analysis

1. Introduction

The deep concern to ensure safe air travelling is the primary reason why structural elements of the "hot" aircraft engine parts are subject to quite exceptional requirements as regards both the manufacturing process and quality control regime. At present, the near-net-shape castings of the aircraft engine parts are made from modern grades of nickel and cobalt alloys, like INCONEL 100 , INCONEL 713C, RENE 77, MAR-M257 and MAR M 509 [1, 2]. These alloys are precipitation hardened, and on solidification they produce a specific type of macrostructure composed of frozen and columnar equiaxial grains. A structure of this type is sensitive to crack formation and propagation, which can result in fatal failure of the aircraft engines [3, 4].

The technical world literature explains *in extenso* various possibilities to improve the microstructure of nickel superalloys by refining [5] and modification with nanoparticle inoculants [6-9]. So far, nickel alloys which are the subject of the present study have not been manufactured in Poland. The remelting processes for alloy refining and recovery have not been carried out, either. The problem particularly important is the management of post-production waste (rejects, parts of the gating system, etc.). Yet, to make these alloys capable of reuse, it is usually necessary to introduce some alloying elements (especially trace elements) to make up for the losses in chemical composition, and carry out a modification treatment to refine the alloy granular structure. The domestic industry mainly uses imported products. Nickel alloys are cast by very few foundry plants only.

2. Research problem

The main problem discussed in this study was the development of a technology used for refining of post-production waste of selected nickel alloys, with emphasis put on the technique of alloy modification and making up the content of some alloying elements. The surface modification applied so far cannot give fully satisfactory results. The structure on casting cross-section reveals the presence of the undesired columnar crystals. Therefore attempts have been made to develop a technology that would enable simultaneous surface modification (the modifying coating contacts the surface layer of casting) and modification within the whole casting volume.

Basing on the results of studies done so far, the main scope of the research on refining and recovery of post-production waste has been determined, including in particular the following items:

1. Examination of the type series of cast products to select the best three cast alloys (studies undertaken jointly with the WSK-PZL Rzeszów Foundry acting as a consulting body).
2. Writing technical documentation to be used as a basic document in the analysis of melt history („master heat" certificates, chemical composition of castings – post-melting analysis, reports of mechanical tests).
3. Remelting (repeated four consecutive times).
4. ATD thermal analysis.
5. Analysis of chemical composition obtained in individual melts.
6. Structural examinations of individual melts.

The following parameters were considered the best criteria for an evaluation of the remelting process: master heat analysis, the melt history sheets prepared by WSK Rzeszów, the analysis of chemical composition of the recovered melt, macro- and microstructural examinations of selected castings of the aircraft engine vanes, the analysis of post-modification samples of the recovered melts, plotted thermal analysis curves, and the results of mechanical tests (R_m, A_5) combined with hardness measurements.

3. Materials and methods of investigation

Using the results supplied by WSK - PZL Rzeszów, the most commonly cast nickel and cobalt superalloy products were examined. Finally, for tests and examinations done as a part of research task, the following alloys were selected: IN-713C, IN-100 and MAR-247. Altogether, 24 reports of the chemical analysis and mechanical tests were prepared for IN-713C alloy, 11 reports for IN-100 alloy, and 8 reports for MAR-247 alloy.

The results of the analysis:

1. Serious divergences were observed between the values of the chemical analysis stated in certificates („master heat – analysis, Cannon-Muskegon Corp) and obtained on the primary charge ingots by WSK Rzeszów.
2. No systematic analysis of chemical composition has been carried out on ready castings, and therefore it is difficult to determine the melting loss of the main alloying elements.
3. The results of mechanical tests indicate differences even in melts of similar chemical composition.
4. Probably the differences in mechanical properties result from different conditions created for castings on pouring and cooling, and from the effect of surface modification.
5. The same conclusions are valid for the fatigue test results.
6. The analysis of relevant data shows that the melting and casting technology used so far by the WSK Rzeszów Foundry to manufacture cast nickel alloy products should be re-examined very carefully.

The content of the main elements in the examined alloys is compared in tables below. The data were taken from the „master heat"certificate.

IN-713C – Heat 7V1532

C	Cr	Al	Co	Ti	Mo	Hf	W	Zr	Nb	Ta
O,19	13,52	6,13	<0,1	0,83	4,21	<0,5	<0,1	0,06	2,19	<0,05

MAR-247 – Heat 3V4253

C	Cr	Al	Co	Ti	Mo	Hf	W	Zr	Nb	Ta
0,15	8,33	5,59	10,0	1.00	0,65	1,40	9,98	0,032	<0,05	3,17

IN-100 – Heat 3V4101

C	Cr	Al	Co	Ti	Mo	Hf	V	Zr	Nb	Ta
0,161	8,56	5,66	13,41	4,66	3,01	<0,5	0,80	0,03	<0,05	<0,05

Alloys selected for further investigations were remelted in an Al_20_3 crucible of Balzers VSG-02 furnace. The charge weight was 1,2 kg (the casting weight was 0,8 kg). Melting was carried out under a vacuum of 10^{-3}. Before pouring, the furnace space was rinsed with argon. Pouring was conducted under argon atmosphere at a pressure of 900hPa. After sampling for the chemical analysis and structure examinations, the casting was remelted once again. Altogether four remelting operations were performed. Moulds were preheated to 750^{o}C before being placed in the furnace chamber. The melt/ceramic mould temperature was controlled with an immersion Pt-PtRh10 thermocouple. The mould pouring temperature was 1470^{o}C. For ATD thermal analysis, a modern Crystaldigraph PC-8T apparatus was used.

The test casting was designed as a bar shown in Fig. 1. The temperature measurement and ATD analysis were carried out at 1/3 of the casting height (counted from the bottom). Figure 2 shows the investment ceramic moulds after readjustments made by the WSK Rzeszów, while Fig. 3 shows the ceramic mould placed in the chamber of induction furnace.

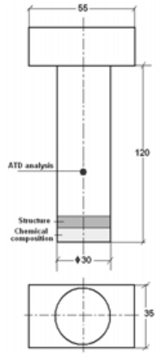


Fig. 1. Test casting

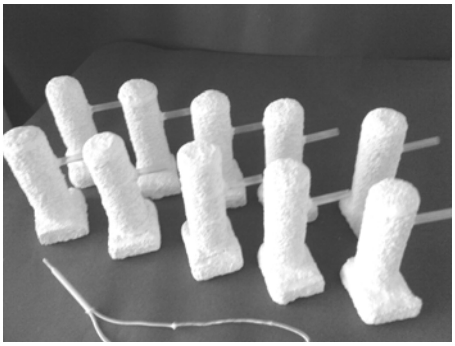


Fig. 2. Ceramic moulds

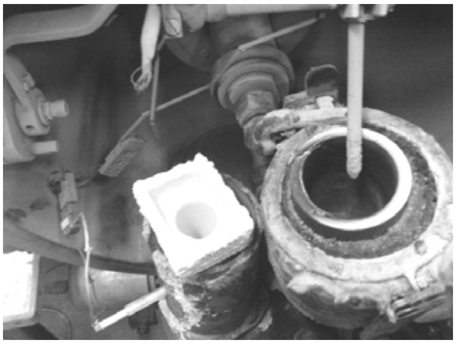
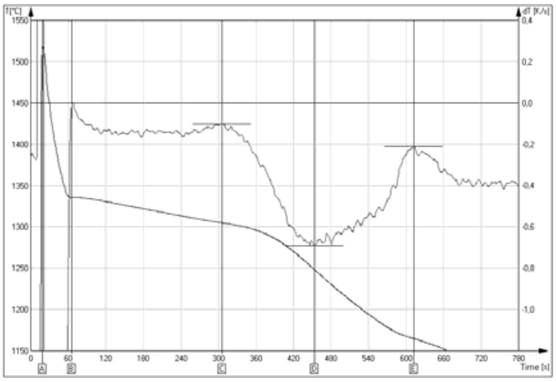


Fig. 3. A view of Balzers VSG-02 induction furnace chamber

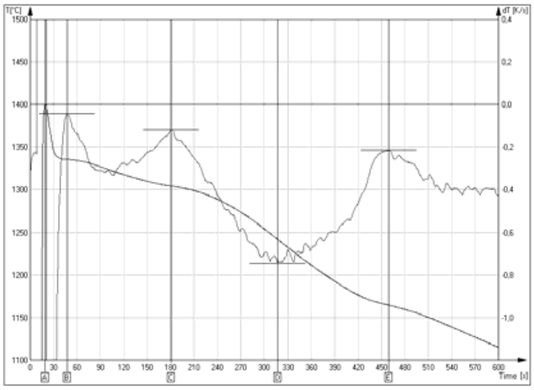
4. The results of investigations and discussion of results

The example of thermal analysis done on a specimen of IN-713C alloy from the "master heat" after remelting 2, 3 and 4 is shown in Figs. 4 , 5 and 6.



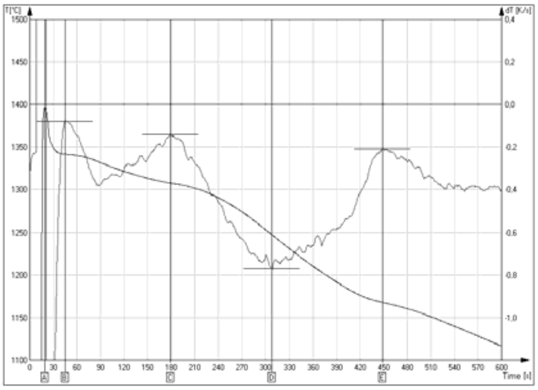
T_{max}	[A]	19 [s]	1518 [°C]
T_{lik}	[B]	66 [s]	1336 [°C]
T_{Eut}	[C]	306 [s]	1305 [°C]
T_{sol}	[D]	454 [s]	1248 [°C]
T_{pst}	[E]	613 [s]	1165 [°C]

Fig. 4. Plotted curve of ATD analysis and values measured at points characteristic of IN-713C alloy after remelting 2



T_{max}	[A]	20 [s]	1400 [°C]
T_{lik}	[B]	48 [s]	1336 [°C]
T_{Eut}	[C]	181 [s]	1304 [°C]
T_{sol}	[D]	317 [s]	1242 [°C]
T_{pst}	[E]	460 [s]	1165 [°C]

Fig. 5. Plotted curve of ATD analysis and values measured at points characteristic of IN-713C alloy after remelting 3



T_{max}	[A]	20 [s]	1387 [°C]
T_{lik}	[B]	45 [s]	1342 [°C]
T_{Eut}	[C]	179 [s]	1308 [°C]
T_{sol}	[D]	308 [s]	1247 [°C]
T_{pst}	[E]	449 [s]	1168 [°C]

Fig. 6. Plotted curve of ATD analysis and values measured at points characteristic of IN-713C alloy after remelting 4

The collective results obtained from all remelting operations are compared in Table 1.

The symbols denote:

T_{max} – the maximum temperature on ADT curve,

T_{lik} – the temperature of the beginning of metal matrix solidification,

T_{Eut} – the temperature of the beginning of carbide eutectic solidification,

T_{sol} – the temperature of the end of alloy solidification,

T_{ps} – the mean temperature for the solid state γ to γ' transformation.

Table 1. Solidification parameters obtained for individual melts

Alloy	Remelting	T_{max} ^oC	T_{lik} ^oC	T_{Eut} ^oC	T_{sol} ^oC	T_{pst} ^oC
IN713C	1	1445	1338	1308	1246	1166
	2	1518	1336	1305	1248	1165
	3	1400	1336	1304	1242	1165
	4	1387	1342	1308	1247	1168
MAR247	1	1418	1364	1350	1275	1212
	2	1421	1368	1352	1283	1213
	3	1425	1364	1345	1280	1210
	4	1402	1352	1338	1273	1205
IN100	1	1422	1326	1314	1255	1219
	2	1429	1327	1309	1255	1222
	3	1435	1327	1310	1256	1220
	4	1442	1326	1312	1257	1222

The results of thermal analysis indicate that the solidification parameters undergo only very small changes from melt to melt, and hence it can be expected that the chemical composition will also remain relatively stable.

To sum up, the following conclusions have been drawn:

1. An empirical relationship can be developed. between the temperature T_{lik} and the content of main elements in the examined alloys This is particularly true in the case of IN-713C and IN-100 alloys. The temperature T_{lik} for MAR-257 is higher by 15 to 20°C, due to the presence of 10% tungsten in alloy composition.
2. No thermal effects resulting from the precipitation of primary phases, carbides in particular, were observed on the ATD curves.
3. Basing on the results of thermal analysis it can be concluded that pouring temperature used by the WSK Rzeszów Foundry is too high for these alloys (1500°C).
4. From the investigations carried out so far it follows that pouring temperature should be established individually for each alloy grade.
5. The temperature T_{sol} for IN-713C alloy is approximately 1242°C, which indicates possible surface melting of the carbide eutectic during heat treatment.

The chemical analysis was carried out on a Foundry-Master Compact 01L00113 emission spectrometer. The results of the analysis after successive remelting operations are shown in Figs. 7 to 16.

Closer look at the obtained results indicates the following:

1. IN-713C alloy
   - the successive remelting operations have no significant effect on changes in alloy chemical composition,
   - only aluminium content is slightly reduced (melting loss),
   - the above statements are confirmed by the results of ATD thermal analysis (stabilisation of T_{lik}, T_{Eut}, T_{sol} and T_{pst}).
2. MAR-247 alloy
   - the successive remelting operations change the alloy chemical composition,
   - the content of Cr, Ta, Hf, and especially of C (!) is reduced (melting loss),
   - the above statements are confirmed by the results of ATD thermal analysis (well visible drop in the values of T_{lik}, T_{Eut}, T_{sol} and T_{pst}, especially after remelting 4).
3. IN-100 alloy
   - the successive remelting operations have no significant effect on changes in alloy chemical composition,
   - only the content of Al, Ti, and especially of C (!), is slightly reduced (melting loss),
   - the above statements are confirmed by the results of ATD thermal analysis (T_{lik}, T_{Eut}, T_{sol} and T_{pst}).
4. It would be worthwhile to think about possible causes of so large divergences between the results of the analysis of Co, C and Si content and values claimed by conformity certificates.

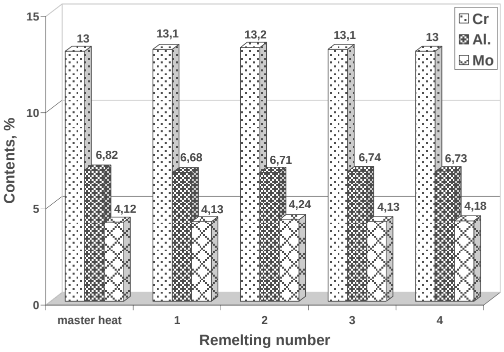


Fig. 7. IN-713C alloy. Change in Cr, Al and Mo content

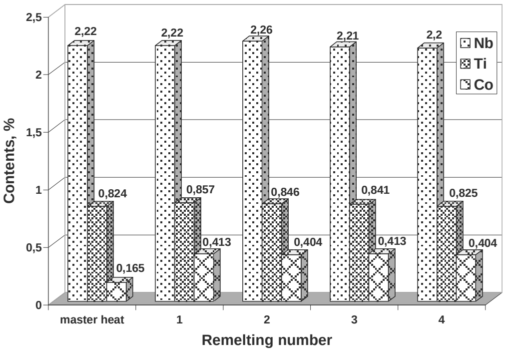


Fig. 8. IN-713C alloy. Change in Nb, Ti. and Co content

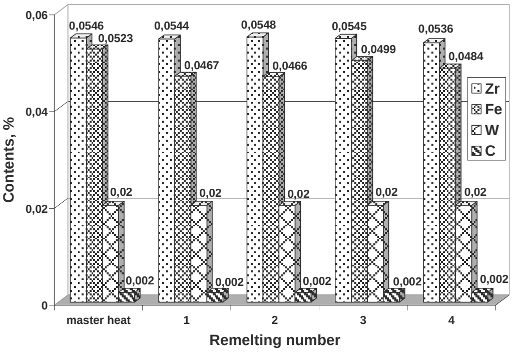


Fig. 9. IN-713C alloy. Change in Zr, Fe., W and C content

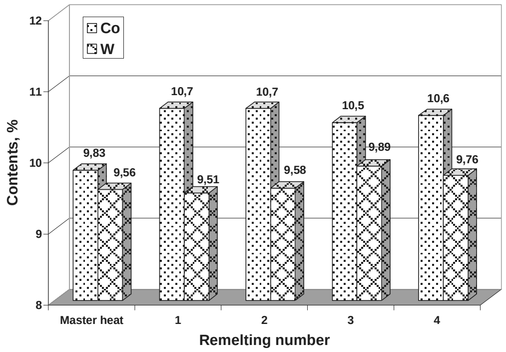


Fig. 10. MAR-247 alloy. Change in Co and W content

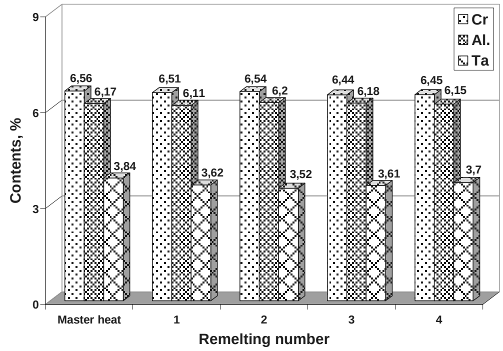


Fig. 11. MAR-247 alloy. Change in Cr, Al and Ta content

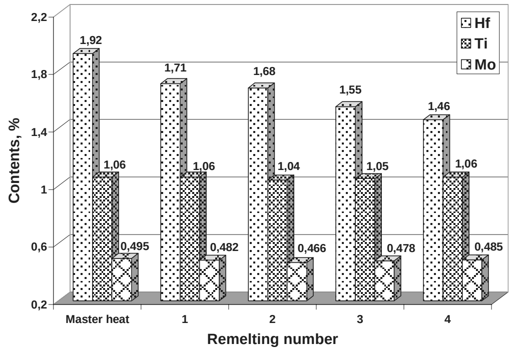


Fig. 12. MAR-247 alloy. Change in Hf, Ti and Mo content

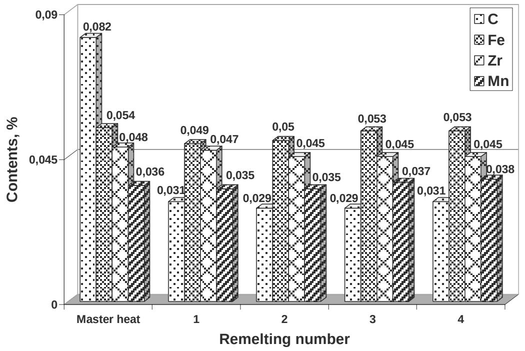


Fig. 13. MAR-247 alloy. Change in C, Fe, Zr and Mn content

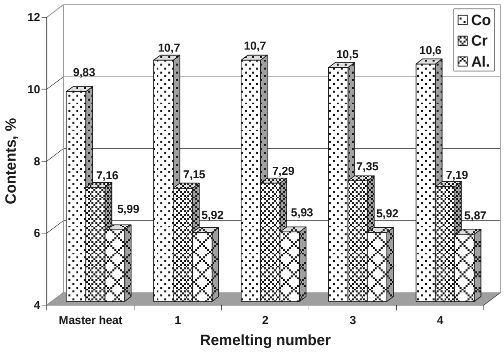


Fig. 14. IN-100 alloy. Change in Co, Cr and Al content

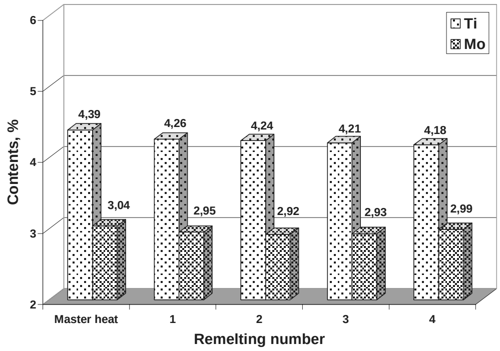


Fig. 15. IN-100 alloy. Change in Ti and Mo content

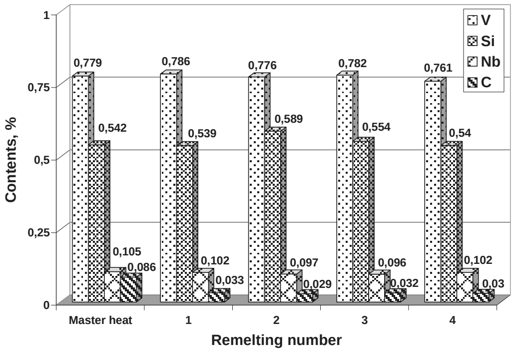


Fig. 16. IN-100 alloy. Change in V, Si, Nb and C content

Specimens for macrostructural examinations were etched with Marble reagent. The examples of the results obtained for specimens in primary condition and after fourth remelting are shown in Figs. 17 to 19.

The specimens for microstructural examinations were etched with Kallings reagent no. 1 (1,5 g $CuCl_2$, 33 ml H_2O, 33 ml HCl, 33 ml C_2H_5OH). Examinations were carried out under a Nikon Epiphot 200 optical microscope. The results of these examinations obtained for MAR-247 alloy are shown in Fig. 20.

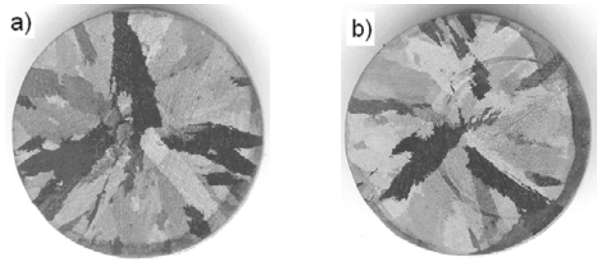


Fig. 17. Macrostructure of casting made from IN-713C alloy in primary state (a) and after fourth remelting (b)

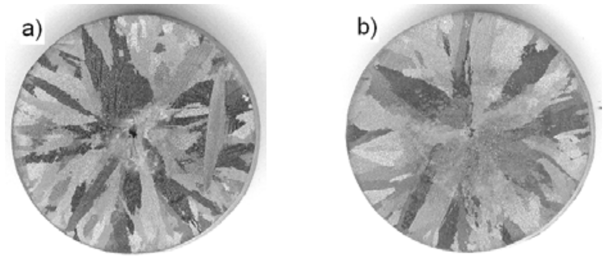


Fig. 18. Macrostructure of casting made from MAR-247 alloy in primary state (a) and after fourth remelting (b)

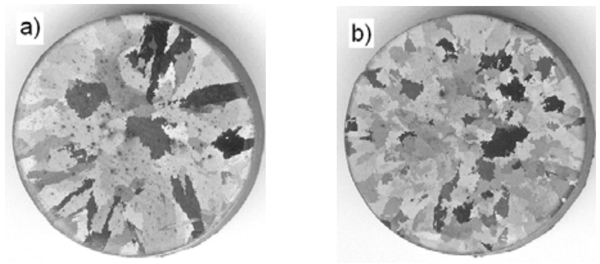


Fig. 19. Macrostructure of casting made from IN-100 alloy in primary state (a) and after fourth remelting (b)

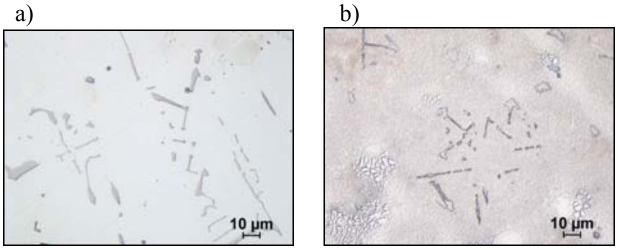


Fig. 20. Microstructure of casting made from MAR-247 alloy in primary state (a) and after fourth remelting (b)

From the examinations of alloy structure the following conclusions follow:

1. Macrostructural examinations tell us how important the conditions of casting pouring and solidification really are. Because of small capacity of the Balzers furnace (about 1,2 kg), keeping the pouring temperature at a constant level is practically not possible. Mould temperature is also unstable at the time of pouring. The consequence are serious variations in alloy macrostructure (grain size).
2. IN-713C and MAR-247 alloys show the presence of a large zone of columnar crystals.
3. IN-100 alloy is characterised by natural tendency to the formation of equiaxial crystals. This is particularly well visible in alloy from the fourth remelting.
4. Compared to primary state, the microstructure of the examined alloys changes after remelting (the „master heat" specimen is used as a reference sample). After remelting, primary carbides disappear as a result of carbon content reduced in respect of the „master heat" specimen
5. The successive remelting operations do not change in a significant way the image of alloy microstructure. Variations in pouring and cooling conditions affect the size of eutectic precipitates.

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