THERMODYNAMIC STABILITY
OF AUSTENITIC Ni-Mn-Cu CAST IRON

The performed research was aimed at determining thermodynamic stability of structures of Ni-Mn-Cu cast iron castings. Examined were 35 alloys. The castings were tempered at 900 °C for 2 hours. Two cooling speeds were used: furnace-cooling and water-cooling. In the alloys with the nickel equivalent value less than 20,0 %, partial transition of austenite to martensite took place. The austenite decomposition ratio and the related growth of hardness was higher for smaller nickel equivalent value and was clearly larger in annealed castings than in hardened ones. Obtaining thermodynamically stable structure of castings requires larger than 20,0 % value of the nickel equivalent.

Key words: austenitic cast iron, heat treatment, structure martensitic transition, cooling, nickel equivalent

INTRODUCTION

The Ni-Resist cast iron is a typical representative of alloys with austenitic structure, stable within wide temperature range. This is a high-nickel cast iron containing 18 to 36 % of Ni [1, 2]. There is a possibility to reduce nickel content by replacing it partially by manganese and copper – the elements that stabilize austenite, like nickel does [3, 4]. A basic problem of this solution is determining acceptable limits of this replacement.

Obtaining austenitic structure of castings requires introducing to the alloy suitably big total fraction of elements inhibiting the transitions that can occur during non-equilibrium cooling-down of castings. These elements, mainly due to reduced diffusion rate of carbon in austenite [5], must shift the eutectoid [6] and bainitic [7] transition areas in the Time-Temperature-Transformation (TTT) diagram to the right effectively enough, as well as to reduce the martensite start temperature M_S below the lowest working temperature of the castings [8]. The necessary total content of alloying elements is determined by minimum value of the nickel equivalent Equ_{Ni}. Both the calculation way (evaluation of austenite-stabilizing effect of the elements) and the required minimum equivalent value are presented in literature in ambiguous way [9-11].

In the paper, used is the equation that considers not only concentrations of typical austenite stabilizers (nickel, manganese and copper), but also carbon and silicon [12]:

$$Equ_{Ni} = 0,32\ C + 0,13\ Si + Ni +$$
$$+\ 2,48\ Mn + 0,53\ Cu\ /\ \% \qquad (1)$$

Austenitic structure of raw castings is obtained, when concentration of this equivalent is higher than 16 %. In a casting with the equivalent slightly lower than 16 %, austenite can be thermodynamically unstable. This can lead to changed microstructure of the castings utilized at elevated temperatures. So, there is a need to find the minimum equivalent value that permits obtaining thermodynamically stable austenite. This is an important question, e.g. in bimetallic castings of pistons equipped with cast-iron inserts.

PURPOSE AND SCOPE OF THE RESEARCH

The performed examinations were aimed at determining minimum value of nickel equivalent Equ_{Ni} required to obtain stable austenitic structure of castings utilized at elevated temperatures.

The examinations were executed on 35 cast iron castings, with chemical compositions given in Table 1. The eutectic saturation ratio S_C ranged between 0,80 and 1,50, and the nickel equivalent [calculated acc. to (1)] ranged between 16,0 and 30,0 %. The castings (standard shafts dia. 30 mm) were made in shell moulds. Raw castings were subject to two kinds of heat treatment:
- tempering at 900 °C for 2 hours followed by furnace-cooling (annealed castings)
- tempering at 900 °C for 2 hours followed by water-cooling (hardened castings).

The examinations included: metallographic observations, Wavelength Dispersive Spectroscopy (WDS) chemical analysis, dilatometric tests, Brinell hardness measurements and Vickers microhardness measurements of structural components.

RESULTS

All the castings in as-cast condition showed austenitic structure of metallic matrix. Quantity and features

A. Janus, M. Stachowicz, Wroclaw University of Technology, Department of Foundry Engi-neering and Automation, Wrocław, Poland

Table 1 **Chemical composition of the examined cast iron**

| Element	Concentration / %		
	min.	max.	average
C	2,6	5,0	3,6
Si	1,3	2,8	2,1
Ni	2,1	9,5	6,5
Mn	1,9	7,6	4,4
Cu	0,1	5,7	2,8
P	0,12	0,15	0,14
S	0,03	0,05	0,04

of graphite changed depending on the S_C value, from fine particles (distribution type D and E acc. to ISO 945) in the alloys with the lowest S_C value between 0,80 and 0,85 to large primary particles (distribution type C) in the alloys with the S_C value between 1,40 and 1,50. Hardness of the alloys ranged from 90 to 130 HB as a result of graphite content and austenite hardness (205 to 225 $HV_{0,05N}$).

Tempering the castings at 900 °C for two hours was aimed at obtaining equilibrium state. It caused partial decomposition of austenite in the alloys with the nickel equivalent below 20 %. The decomposition ratio decreased along with decreasing Equ_{Ni} value and was visibly higher in annealed castings than in hardened ones. Figure 1 shows structures of the casting with Equ_{Ni} equal to 19,3 % in annealed (a) and hardened (b) condition. As a result, in comparison with hardness of the raw casting (110 HB), hardness of the annealed casting increased by 50 HB units (to 160 HB) and that of the hardened casting increased by 10 HB units (to 120 HB).

Figure 2 shows the case of maximum decomposition ratio of austenitic structure of a raw casting with Equ_{Ni}
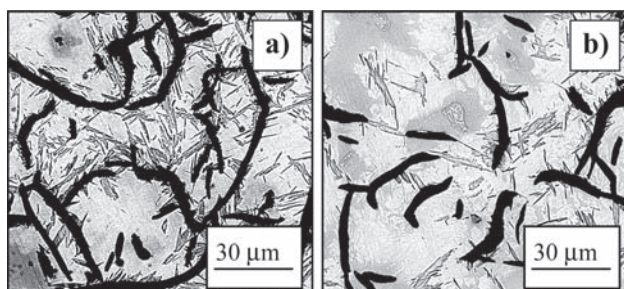
Figure 1 Partial decomposition of austenite: a) in annealed casting and b) in hardened casting. Composition of the alloy: 3,4 % C, 2,0 % Si, 6,2 % Ni, 4,2 % Mn, 2,5 % Cu
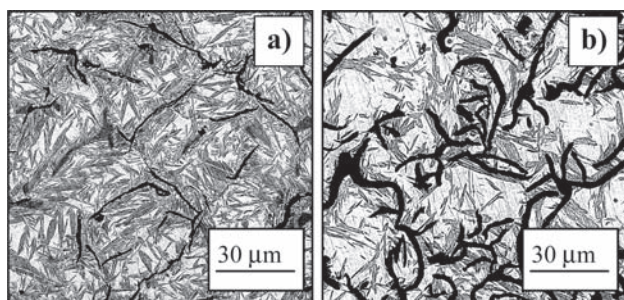
Figure 2 Decomposition of austenite: a) in annealed casting and b) in hardened casting. Composition of the alloy: 3,1 % C, 1,8 % Si, 5,9 % Ni, 2,9 % Mn, 3,4 % Cu

equal to 16,1 %. After annealing, 90 % of austenite is decomposed, which results in hardness increase by 200 units – from 135 HB for the raw casting to 335 HB for the annealed casting. The austenite decomposition ratio in the hardened casting is slightly lower, equal to 75 %. Smaller is also hardness increase amounting to 75 HB units.

Increase of austenite hardness is caused by martensite created during cooling-down of castings after tempering. The fact that no martensite is present in any of the raw castings but is found in a part of the heat-treated castings, proves that diffusion processes increasing the M_S temperature took place in austenite during tempering. This is confirmed by results of dilatometric measurements. The specimens were heated-up to 900 °C at a rate of 5 °C/min, kept at this temperature for 2 hours, cooled-down at similar rate to - 175 °C (using liquid nitrogen) and then heated-up to ambient temperature. Figures 3 and 4 show dilatograms obtained for 2 alloys with nickel equivalent value being 23,0 % 16,1 %, respectively.

It is well-known that the martensite start temperature M_S of all raw castings is lower than ambient temperature, as evidenced by their austenitic structure. In the alloys with the nickel equivalent value above 20,0 %, total concentration of the austenite stabilizing elements is sufficient to inhibit diffusion of carbon during their tempering and cooling. Thus, the M_S temperature of these alloys is still lower than ambient temperature, see Figure 3.

In the alloys with Equ_{Ni} value below 20,0 %, content of additives is insufficient to inhibit diffusion of carbon, which resulted in increasing the M_S temperature above ambient temperature, see Figure 4.

In order to determine changes of chemical composition of austenite during tempering, WDS analyses were carried-out for the castings in raw condition as well as for the annealed and hardened ones. Analysed were concentrations of elements in austenite (A) and martensite (M). Results are collected in Table 2.

The carried-out analysis demonstrated inverse segregation of nickel and copper, as well as positive segre-
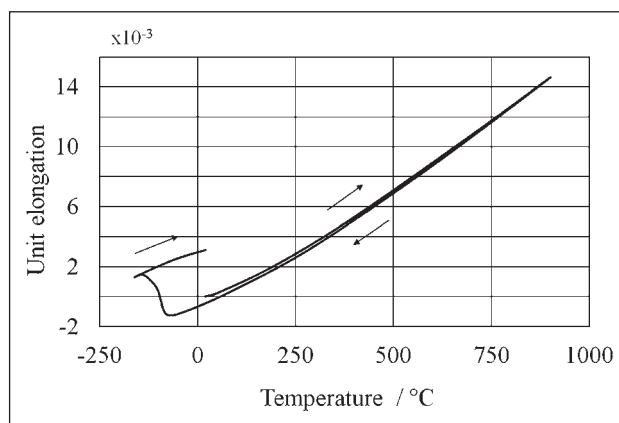
Figure 3 Dilatogram of cast iron containing 3,3 % C, 2,3 % Si, 7,2 % Ni, 5,7 % Mn, 0,5 % Cu; S_C = 1,02; Equ_{Ni} = 23,0 %; M_S = - 85 °C
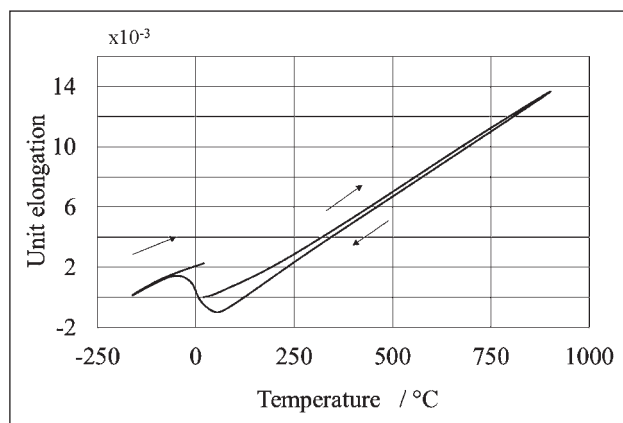
Figure 4 Dilatogram of cast iron containing 3,1 % C, 1,8 % Si, 6,2 % Ni, 3,5 % Mn, 3,5 % Cu; $S_C = 0,98$; $Equ_{Ni} = 16,1$ %; $M_S = 120$ °C

Figure 5 Relationship between Equ_{Ni} and hardness increase of cast iron: ΔHB_A (annealed) and ΔHB_H (hardened)

Table 2 **WDS analyses of alloy containing: 3,4 % C, 1,8 % Si, 3,9 % Ni, 3,6 % Mn, 3,1 % Cu**

Casting	Phase	Concentration / %				
		C	Si	Ni	Mn	Cu
raw	A	0,46	2,0	4,9	2,9	3,8
annealed	A	0,50	2,1	4,7	3,0	3,5
	M	0,28	2,2	4,5	2,6	3,2
hardened	A	0,58	2,3	4,8	3,3	4,0
	M	0,34	2,4	4,4	2,8	3,5

gation of manganese in austenite. This means that, in Ni-Mn-Cu cast iron, the austenite-stabilizing elements complement their inhibiting influence on carbon diffusion. Concentration of carbon itself is heterogeneous. In raw castings, close to precipitates of high-carbon phases (graphite and cementite), concentration of carbon is slightly lower than in centres of austenitic areas. During tempering at 900 °C, carbon segregation ratio in austenite probably increased even further. As a result, martensitic transition took place in the areas with lowered carbon concentration. The remaining part of austenite, enriched in carbon, constitutes thermodynamically stable retained austenite.

Differences of carbon concentration in austenite between an annealed and a hardened casting are related to solubility of carbon in austenite that drops with decreasing temperature (line E`-S` in the Fe-C$_{graph}$ diagram). Slow furnace-cooling of castings permits this process to run in nearly equilibrium conditions (lower austenite stability due to lower carbon concentration). Such a possibility does not exists in the conditions of quick water-cooling, when austenite is more thermodynamically stable. This explains the difference of austenite decomposition ratio between the annealed and the hardened castings.

The differentiated austenite decomposition ratio (related to the nickel equivalent value) affects hardness of the castings. Figure 5 shows hardness increase of the annealed and the hardened castings in comparison to the raw castings.

The alloys with Equ_{Ni} below 16,0 % demonstrate an increase of hardness that clearly intensifies with lower-

ing nickel equivalent value and thus with increasing amount of martensite that is significantly larger in the annealed castings. This is possible during slow cooling, when concentration of carbon in austenite can drop down, M_S temperature can grow higher and austenite decomposition ratio can increase. In the extreme case, hardness of cast iron increases more than twice.
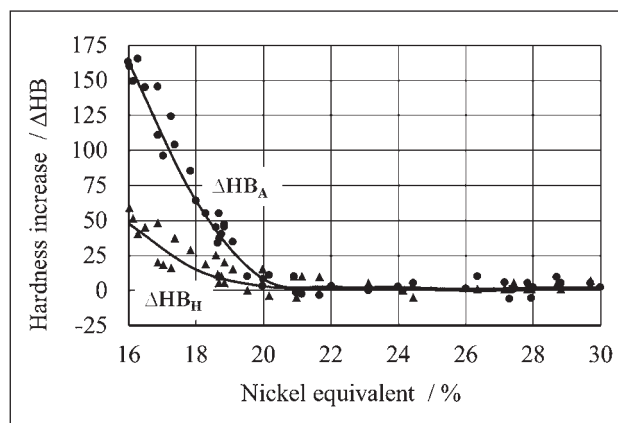
CONCLUSIONS

Austenite that at ambient temperature constitutes structures of raw castings of Ni-Mn-Cu cast iron, can be thermodynamically unstable. Non-equilibrium solidification and cooling conditions present in a casting mould induce strong supersaturation of austenite with carbon. This is intensified by presence of nickel, manganese and copper – the elements mightily reducing diffusion rate. As a result, no transition of primary structure occurs in a cast iron with nickel equivalent exceeding 16 %. In such a case, total content of alloying elements is sufficient to reduce the martensite start temperature below ambient temperature.

However, if diffusion of carbon is started as a result of heating to the sufficiently high temperature (900 °C), tempering time is sufficiently long (2 hours) and content of alloying elements is low enough ($Equ_{Ni} < 20$ %) to allow carbon diffusion, concentration of carbon in austenite drops locally, especially in vicinity of graphite and cementite particles. In consequence, the martensite start temperature M_S in these areas increases above ambient temperature and austenite can be partially transformed to martensite as castings cool down from tempering temperature. The transition ratio is higher for larger values of nickel equivalent, when the M_S temperature is higher.

The final result depends also on cooling rate of tempered castings. Long time of furnace-cooling permits reduction of carbon concentration in austenite according to its decreasing solubility limit. This results in higher martensitic transition ratio. In hardened castings, diffusion of carbon does not keep-up with decreasing solubility limit and austenite again becomes supersaturated with carbon,

thus increasing its thermodynamic stability. For this reason, decomposition of austenite is more complete in annealed castings than in hardened castings.

As a result of changed structure of a casting, its hardness increases proportionally to the portion of martensite. In extreme cases (Equ_{Ni} close to 16,0 %), hardness of castings increases more than twice.

The performed examinations showed that, in the castings solidifying according to the equilibrium system (with no hard spots), thermodynamically stable austenite can be obtained in the alloys with the nickel equivalent value above 20,0 %.

References

[1] Y. A. Alzafin, A.-H. I. Mourad, M. Abou Zour, O.A. Abuzeid, Engineering Failure Analysis, 14 (2007), 1294–1300.

[2] E. Guzik, D. Kopycinski, Archives of Foundry, 12 (2004), 115-121.

[3] A. Janus, S. Chorzępa, B. Ankudowicz, Patent. Polska, nr 174712. Żeliwo stopowe austenityczne. IntCl6: C22C 37/00, 1995.

[4] S. Seyedi, R. Rikhtegar, Journal of Iranian Foudryment`s Society, 14 (1994) 4, 122-136.

[5] C. P. Scott, J. Drillet, Scripta Materialia, 56 (2007), 489-492.

[6] D. M. Stefanescu, Materials Science and Engineering A 413–414 (2005), 322–333.

[7] S.C. Murcia, M.A. Paniagua, E.A. Ossa, Materials Science and Engineering, A 566 (2013), 8–15.

[8] Q. X. Dai, X. N. Cheng, X. M. Luo, Y. T. Zhao, Materials Characterization 49 (2003), 367– 371.

[9] N. G. Girszowicz, Kristalizacija i swojstwa čuguna w otliwkach, Moskwa-Leningrad 1966.

[10] E. Szpunar E., Prace Instytutu Mechaniki Precyzyjnej (1967) 1, 12-25.

[11] A. de Sy, Z. van Eeghem, R`esultatas des recherches sur les fontes amagnetiques au Ni-Mn-Cu, 25-eme Congres Internacionale de Fonderie, Menoire nr 6, Bruxelles 1958.

[12] A. Janus, J. Kaczmar, Acta Metall. Slovaca, 5 (1999) 2, 452-457.