UDK

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ANALYSIS OF TITANIUMMICRO-ALLOYINGINFLUENCE ON PHASE TRANSFORMATIONS INTHE MOTTLED CAST IRONS

This analysis depends on differentialthermal analysisprocesses occurringduring heating in themicro-alloyediron of titanium. Data on the influence of dispersionof the metal matrix, shape and distributionof graphite onthe temperaturephase transition is validated. It was found thatthe titanium inthe rangeinvestigated(0,017...0,044%) shifts the formationof the oxide filmin theregion of lower temperatures. Cast iron's intensive oxidation processes begin at 460-500° C. Therefore, it is seen thattitaniumimpuritiesin the investigatedrange of concentrationscan adversely affectthe heat resistanceof the castings.

Investigationsof the physical natureand the mechanismof Fe-C alloysstructure formation are essential tofor the development ofthe general theory ofalloys andfor solvingthe particular founding forproduction of cast iron. Titaniumis always presentin the cast iron, because it is a native element present in ironore. Titanium is also incorporated into the melt as a contaminant from steel and cast iron waste. The titanium impurities in the materials charge result not only in powerful changes in the expected interatomic interactions but also lead to the emergence ofnoticeablestructural peculiaritiesin the solidmetal.

Analysis of the problem. A small amount of titanium in liquid cast cast iron is observed to favor its graphitization. [1] According to [2], it is somewhat reduces the strength of cast iron, as it neutralizes (binds) nitrogen. Titanium is reducing agent and modifier, which enhances the grindability of the cast iron, increases the dispersivity of the structure and corrosion properties [3, 4]. Titanium at 0.03 - 0.10% is injected into special gray con-

struction cast iron in order to increase theirwear resistance due to the formation of carbides or carbonitrides [5]. It is also noted that titanium is valued as the main element in the carbide in white irons [6].

No data was obtained about processes of phase transitions in cast iron with titanium microdoses occurring at low temperatures, although it is suspected that this may be important in the analysis of the heat resistance of the castings.

The purpose of this research is to study the influence of titanium impurities on phase transitions in mottled cast irons, as well as the performance properties of castings formed through these phase transitions.

*Research methods.*Smelting was conducted on high-frequency setting VCHI10-10/0.44. Weight lump charging: 0.2 ± 0.01 kg. Chemical composition of the base cast iron (% by weight): C 3.14; Si 2.20; Mn 0.61; Cr 0.20; S 0.03; P 0.05. Melting time in a heated crucible: 100±10s. Temperature of the metal in the furnace determined by thermo-couple Pt / Pt recording potentiometer KSP-4.

Any change of state of metals and alloys (phase, inter-phase or structural transformation) is an enthalpy change, and therefore must be accompanied by a thermal effect - preposition or absorption of heat. In researching chemical reactions and transformations that occur under the influence of the heating or cooling of alloys, differential thermal analysis methodology was used to measure small thermal effects. Thermogravimetry was used to determine with great precision the change of mass of the investigated sample in the process transformation [7].

Transformations of the metal can be monitored and calculations with a particular amount of reaction products can be made with the help of the curve of thermogravimetric analysis (TGA) however, differential thermography will improve the quality of TG curve estimates. The curve of the rate of changeof massof the samplein time (DTG) providesreliable datain the studyof the transformations ofthe metal.Simultaneous determination ofthe change in massand enthalpyenables betteranalysis ofthe transformationtaking

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place. Jointthermal andthermal gravimetricanalysis was performedwith the help of derivatography. Experimental technique wasdescribed in work[8].

*Experimental investigations anddiscussions.*Researchon the effect oftitanium on thephase transitions required a series of smelts in which asample ofthe originalcast iron and samples containing increasing amounts of titanium were melted in a furnace heated to 1390-1410° C. Chemical analyses of the smelted samples are shown in table. 1.

Table 1

The experimental meltschemicalcomposition

№№	Element, % by mass (Fe rest)					
	C	Si	Mn	S	P	Ti
Orig. cast iron	3,75-3,80	2,00-2,10	0,61-0,65	0,03-0,04	0,04-0,05	-
1	3,73-3,77	1,79-1,86	0,61-0,65	0,02-0,03	0,04-0,05	0,017-0,019
2	3,60-3,68	2,00-2,15	0,61-0,68	0,03-0,04	0,04-0,05	0,022-0,024
3	3,75-3,80	1,80-1,86	0,60-0,68	0,02-0,03	0,04-0,05	0,030-0,032
4	3,51-3,60	1,72-1,78	0,60-0,68	0,02-0,03	0,04-0,05	0,041-0,044

Thermogravimetricanalysiscurves (TG) showed thatwith the increaseof the titanium contentin the experimentaliron,the onset temperature ofthe incrementof sample massand itsintensiveincreasedeclined(Table2). In the sample of the originaliron, analogous processesoccur at highertemperatures. It was established thattitanium lowers the temperature at which an oxide film develops.

Table 2

The results of thermogravimetric analysis

Parameter	Temperature, °C				
	Original cast iron	T1	T2	T3	T4
Start mass increments	460	450	410	390	370
Intensive growth of mass	750	500	485	480	460

Results of the study. The curves measuring the magnitudeof the thermal effects forthe DTA process vary according to the pattern illustrated in Fig.1:

- On the experimental curves of all samples there are five temperature ranges that have characterized the various processes in the cast iron when heated - I, II, III, IV and V (Table 3);

- Changes in the DTA curves for all samples at temperatures below 300° C are similar in nature;

- Character of the change curves T1 and T4 in the temperature range 300 - 600° C are analogous;

- The shift in the DTA curve in the temperature range 600-800° C for a sample of original cast is comparable to the DTA curve for sample T3

- Curves for T2 and T3 show plateaus that indicate the equality of the thermal effects of the processes taking place.

The structure of the original sample was gray cast iron with lamellar graphite and ferrite-pearlitic matrix. Part IV (see Fig. 1, a) on the DTA curve for this sample is associated with the processes of austenitizing perlite. In austenitizing at this temperature range, eutectoid equilibrium begins when ferrite is oversaturated with carbon and can transition thermodynamically $\alpha \rightarrow \gamma$. As $\alpha \rightarrow \gamma$ transformation is achieved through gradual dissolution of cementite perlites. Further heating (section V) causes dissolution of graphite and polymorphic transformation $\alpha \rightarrow \gamma$, which involves an α solid solution matrix of cast iron, formed by cooling the reaction $A \rightarrow F + G$. Start these transformations needs a higher degree of overheating, increasing the difference between the free phase energies, so they take place at higher temperatures than the austenitizing process perlite. Austenitizing at sites with a perlitic matrix is much faster than in areas with a ferritic matrix [9]. Above the eutectoid range (metastable and stable equilibrium) perlite and ferrite are transformed into austenite, which on further heating becomes further enriched with carbon (due to increasing solubility of carbon in austenite) as a result of dissolution. Part I of the DTA curvesmay be associatedwith processes of gas absorptionandstress relaxationnear thegraphite inclusions.The fastestrelaxationpeak stressesarein the cast ironplateswith coarsegraphite,and the slower arein cast ironwith graphitecompact form[10].With the introduction of0,041%Ti, the number of

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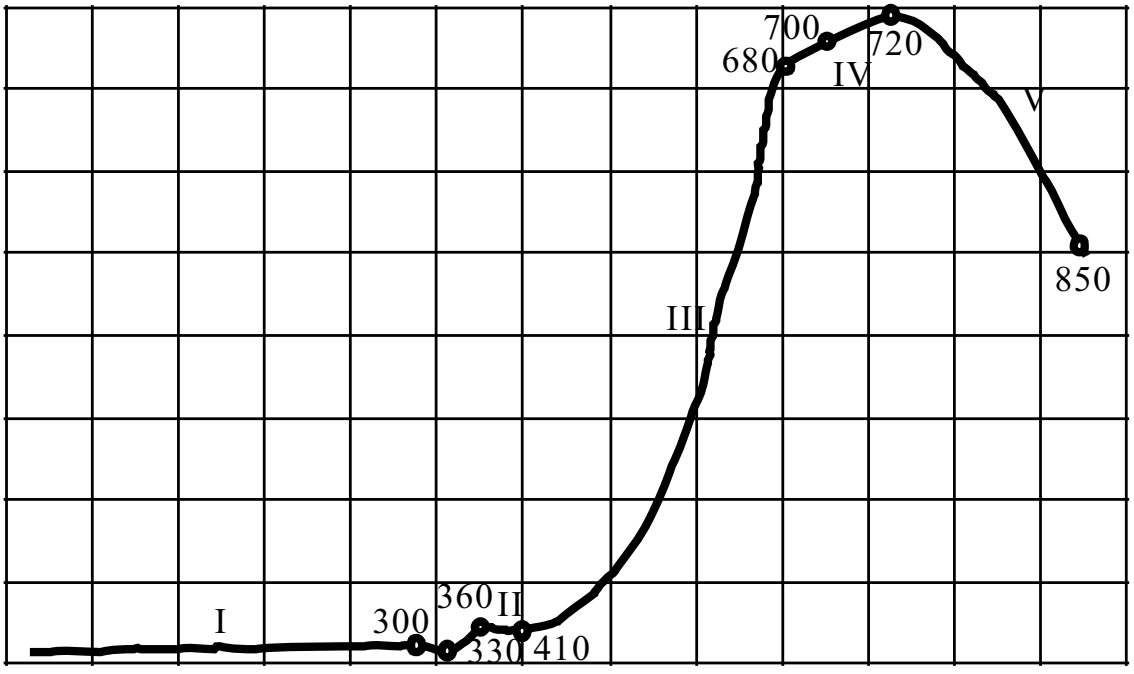
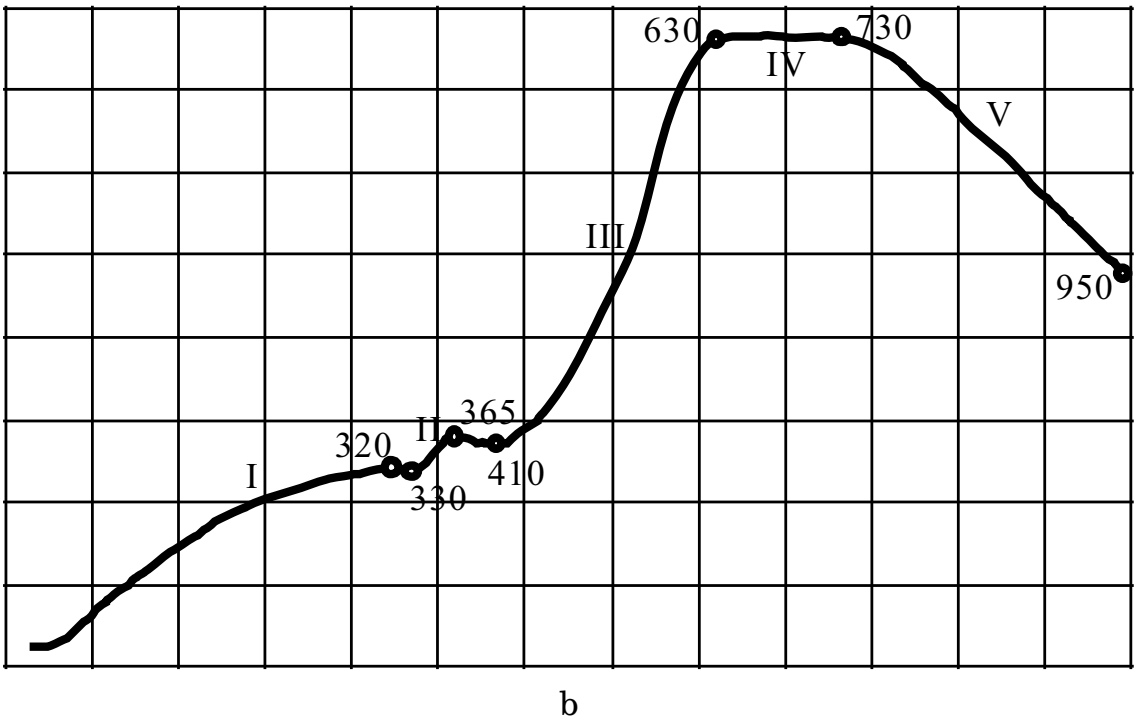
coarsegraphiteplatesdecreasedand the structure was basicallydominated byvorticity graphitewithinterdendriticdistribution. The possibility of thisprocess is demonstrated by the DTA curveon the partIin the sampleT4- it is flatter indicating a decrease inintensity.

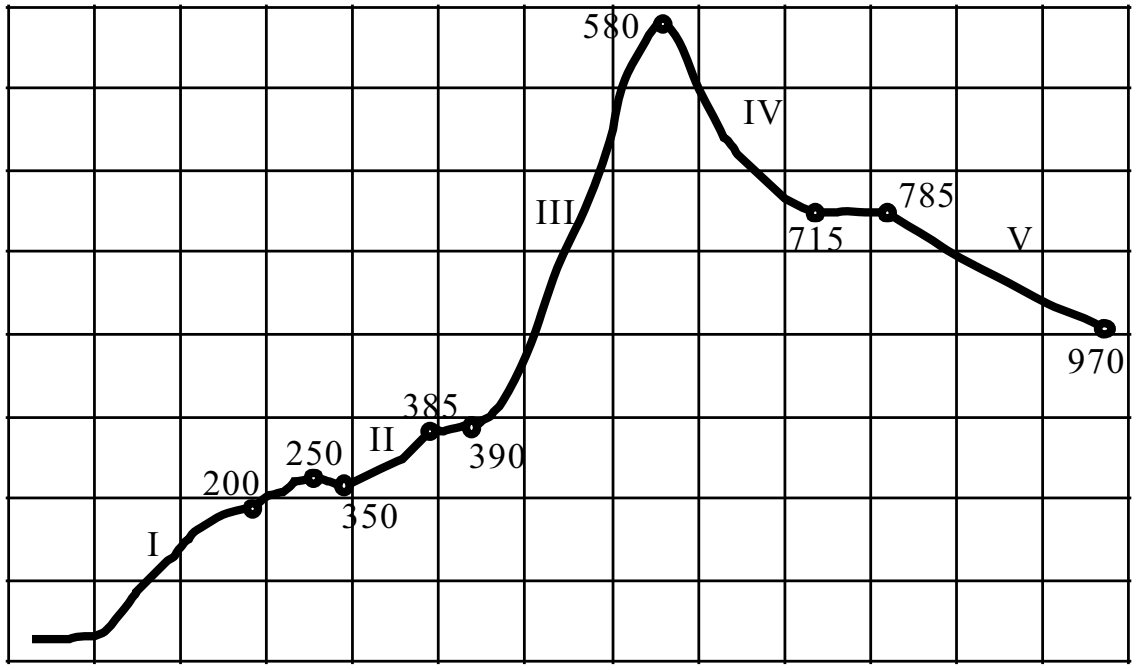


a

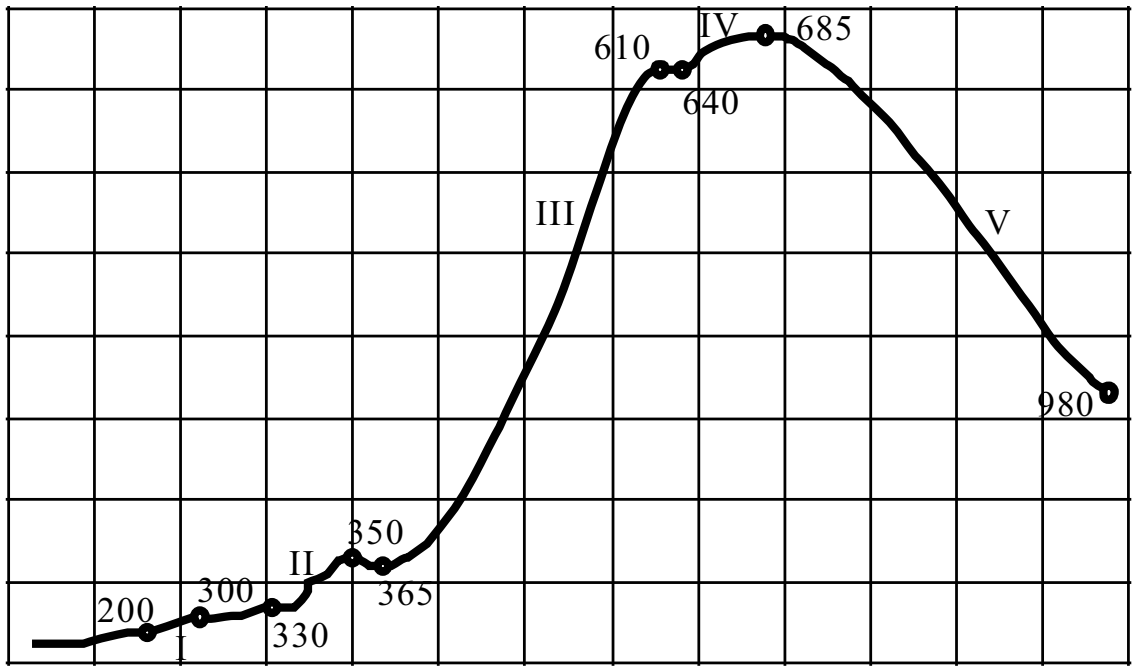


b

Figure 1 - DTA curves ofpilot melts:
a – 0,017...0,019 % Ti;
b – 0,022...0,024 % Ti



c



d

Figure 1 - DTA curves ofpilot melts:
c – 0,030...0,032 % Ti;
d – 0,041...0,044 % Ti

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Table 3

DTA curvesanalysis

№ Sample	Temperature interval and Q* Process				
	I	II	III	IV	V
Initial sample	0-40-60	60-130-340	340-610	610 - 710 - 820	820-900
	Q	+ Q	- Q	- Q	- Q
T1	0-(250)-300	300-360	410-680	680 - 700 - 720	720-850
	+ Q	- Q	- Q	+ Q	- Q
T2	0-320	320-355	355-630	630 - 730	730-950
	+ Q	- Q	- Q	Q	- Q
T3	0-200	250-350	350-580	580-715; 715-785	785-970
	+ Q	- Q	- Q	+ Q - Q	- Q
T4	100-200-300	300-330	330-610	610-640; 640-685	685-980
	Q	Q	- Q	Q + Q	- Q

Notices:

-Q -process occurs withdecreasing temperatureandheat absorption;

Q -the process occurs atconstant temperature with the absorption of heat;

+Q -process occurs withincreasing temperature andheat.

PartsIIandIIIare identifiedwith the processes that occur with variations in dispersionperlite. Parts IV andV show the processes of austenitizingperliteand dissolutionof graphite.According topublished data[9], titanium shifts position of the critical points C' / E' /, S' /, to lower concentrations of carbon.The positiveeffect of smallamounts of titanium(less than 0.1%) on the graphitization is connected with the factthat thecarbideTiCisa substrate for graphite nucleation.

The introduction oftitaniumin the cast ironslows downthe perlite transformation, increasing the stability ofsolidifiedaustenite. The natural increase in stabilityof solid austeniteunder the influenceof alloying elementsis rather complicated.Alloying elementscan slowperlitetransformationfor several reasons:

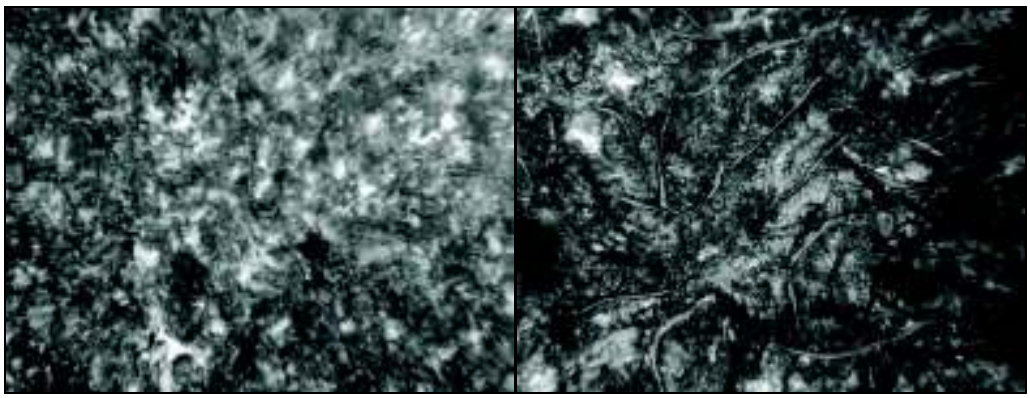
- As aresult of the formation of special carbides. Formation of the austenitenecessitates diffusionary redistributionof alloying elementswhose atoms areless mobile thanthe carbon atoms.

- Through slowing downthe diffusionof carbon;

- Through decreasing the speedof polymorphictransformation $\gamma \rightarrow \alpha$.

According to [11], titaniumcoarsensinperlite eutectoidtransformation. Research [12] hasalso established that for Ti content between 0.41 and 0.44%, perlitebecamehomogeneous.

The microstructureof experimentalcast ironconsists of graphite, perlite and a very small amountof cementite(less than 0.5%). However, the amount, form,distribution ofgraphite,as well as thedispersion andhomogeneityof perlite vary.Fig.2 shows thetypicalstructure.



a b

Figure 2 - The microstructureof the metal matrixof the experimentalcast ironsx 300: a - Ti 0,017 ... 0,019%;b- Ti 0,041 ... 0,044%

In experiments, cast ironsgraphite formedascrystals (graphiteeutecticand possiblyin samplesT1 andT4primarygraphite) and in the solid state(graphitesecondary, but in small volumes andeutectoid). However, econdary graphiteand graphiteeutectoid did not form independent structuralcomponents; they superimposed oncarbonalready presentin the structure.

Austenitizing of ferritestarts with an oversaturationof carbon, when repackingof the iron atoms (transition $\alpha \rightarrow \gamma$) becomes thermodynamicallypossible.Austenite crystalizes andgrowsin perlite, with austenitefirstsaturatedwith carbon, which comes mainly fromdissolvingcementite. During of polymorphic transformation cementite is dissolving first

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and then graphite. At further heating (section V) secondary graphite dissolves GII → A.

Structural changes incast iron withperliticmatrixin the temperature rangeof eutectoid transformation are connected withaustenitizingperlite andcarburizationmatrix. The speed of theseprocesses dependson the composition ofcast iron, the structureof the matrix, the number and branching ofgraphite inclusions, the degree of microscopical segregationof impurities.In [9], the author described the influence of the formof graphite onaustenitizingprocesscast iron. In cast irons with large plate graphite, dissolution is difficult because no good contact with metal matrix. In the cast irons with a highly branched graphite probability of contact loss is lower and degree of impurity segregation (silica) is less. Besides points of α → γ - transformation arise more, and carbon diffusion ways are shorter. This results in high speedaustenitizingand carburizationaustenite, and the contraction ofrangeof the process.

Changing thetemperature of the beginningaustenite formationandgraphitesecondarystartdissolutionwith increasingtitanium contentis presented in Table. 4.The analysis suggeststhat the increaseof the titanium contentin the ironto 0.032% lowers the temperature at which the process of austenitizingperlite begins andincreases the temperature at which the dissolutionof secondarygraphite begins, in this wayexpanding the range of perlitetransformation. Further increaseof the titanium contentto0.041…0.044% leads to a contractionof thetemperature range.

Table 4

Start temperatures of austenite formationand graphitedissolution

Temperature, °C	Titanium content, % (by mass)				
	Original cast iron	0,017...0,019	0,022 ...0,024	0,030... 0,032	0,041...0,044
Begin of education of austenite	610	680	630	580	610
Start dissolving graphite secondary	770	720	730	785	685

The differencesin theDTA curvesin partsIVandVcan be explained bythe difference inthe form anddistributionof graphite,which were notedin samples withdifferent contents oftitanium [3].

As thedispersion of thestructureof graphiteandpearlite increases,austenitizingtimedecreases.The speed ofthis process is proportionalto the diffusion coefficientof carbon andthe concentration gradientnear the boundary at the interface ofF / EandF /C,as well as inareaswith graphite.Therefore, an increase in titanium contentto0.041…0.044%,which increasesthe proportionof graphite inthe form of smallsubeutectic-type vortices enhancesaustenitizingandpromotes decreases inthe temperature differences indicated in sectionIV.Difficultiesin separatingeutectoidand secondary graphite prevent us from calculatingthe volume fraction ofcast ironin the structure as titanium content varies. It can be assumedthat the differencein the curvesTDAin partsIVandV isdue to differences inthe form anddistributionof graphite: The influence of theseparameters on thekinetics of austenitizing anddissolution ofandgraphite leads to differenttotal magnitudeof the thermal effectwhen heatedin the temperature range from 680 to 980°C.

Conclusions

The investigations establish the possibility thatthe experimentaltitanium concentrationhad no effecton the process ofgas absorptionandstress relaxationnear thegraphite inclusionsin the temperature rangeup to 300°C.

Data on the influenceof dispersionof the metal matrix form anddistributionof graphite onthe temperature phase transition has been validated. Titanium content up to 0.032% lowersthe temperature at whichperlite andaustenitizingtemperatureincreasesstartdissolutionof secondarygraphite, henceexpands the range forperlite transformation. Further increaseof the titanium contentto0.041…0.044% results in smallinterdendriticgraphite particles with coarsening ofperliteand thereforeto contractionof thetemperature range.

Titanium contents in the investigatedrange(0.017…0.044%) shift the formationof the oxide filmto lowertemperatures: In the experimentalcast irons,intensive oxidationprocesshas already begunat 460…500°C.Thereforetitaniumimpuritiesin the studiedrange of concentrationscan adversely affectthe heat resistanceof the castings.

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