



Impact of Ti and Fe on the Microstructure and Properties of Copper and Copper Alloys

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Abstract

The paper discusses issues related to the technology of melting and processing of copper alloys. An assessment was made of the impact of titanium and iron introduced in the form of pre-alloy - Ti73Fe master alloy on the microstructure and selected properties of pure copper and copper-silicon alloy. There are known examples of the use of titanium and iron additive to the copper alloy. Titanium as an additive introduced to copper alloys to improve their properties is sometimes also applicable. In the first stage of the study, a series of experimental castings were conducted with variable content of Ti73Fe master alloy entering copper in quantities of 5 %, 15 %, 25 % in relation to the mass of the metal charge. In the second stage, a silicon additive was introduced into copper in the amount of about 4 % by weight and 0.5 % and 1 % respectively of the initial Ti73Fe alloy. Thermodynamic phase parameters were modelled using CALPHAD method and Thermo-Calc software, thus obtaining the crystallization characteristics of the test alloys and the percentage of structural components at ambient temperature. Experiments confirmed the validity of the use of Ti73Fe master alloy as an additive. The pre-alloy used showed a favourable performance, both in terms of addition solubility and in the area of improvement of strength properties. Changes were achieved in the microstructure, mainly within the grain, but also in the developed dendrites of the solid solution. Changes occur with the introduction of titanium with iron into copper as well as to two-component silicon bronze.

Keywords: Copper alloys, Thermodynamic modelling, Alloying additions, Titanium, Mechanical properties, Microstructure

1. Introduction

Copper is one of the most expensive and hardly available metals. This element is characterized by several valuable properties, thanks to which it is widely used in technology. Efforts are being made to develop copper alloys by improving their properties [1-3]. This is associated with increased tensile and bending strength, improved plasticity and even their thermal resistance. Attempts are also being made to improve corrosion resistance and maintain high electrical conductivity. Such improvements can be achieved in a number of ways, e.g. by heat

treatment, modification and by the introduction of appropriate alloying additives [4-7].

Copper alloys with small alloying element additions such as Ag, Be, Cd, Co, Cr, Fe, Ni, Zr, up to 5 % are called alloy copper, and above 5 % - copper alloys. They are used in industry - from chemical equipment, electronic tubular elements, solder nozzles, gas nozzles, radars and telecommunications and radio technical equipment [7,8]. Copper with iron [9-13], chrome [14-19], nickel [20-23] and titanium [24-32] are most commonly used. Copper with magnesium [33] or copper with zirconium [34] are less frequently used.

Titanium copper - the maximum solubility of titanium in copper is 8 % at 885 °C (Figure 1.). Metastable intermediate

phases with an ordered structure may arise in this range before the release of the βTiCu_4 equilibrium phase particles. Between the melting point of the TiCu phase particles and the eutectic transition temperature (73 % at Cu) there are peritectic reactions leading to the formation of intermetallic phases with stoichiometric formulas of Ti_3Cu_4 (57.1 at. Cu), Ti_2Cu_3 (60 at. Cu), TiCu_2 (66,7 at. Cu) i TiCu_4 (78-80.9 at. Cu) [8, 35, 36]. Cu-Ti alloys are an interesting material for foundry in the form of master alloys (pre-stops) for the correction of composition, as well as for the implementation of casting alloy modification procedures. Alloys containing CuTi10 as well as compound alloys [8, 30], among other things, are used.

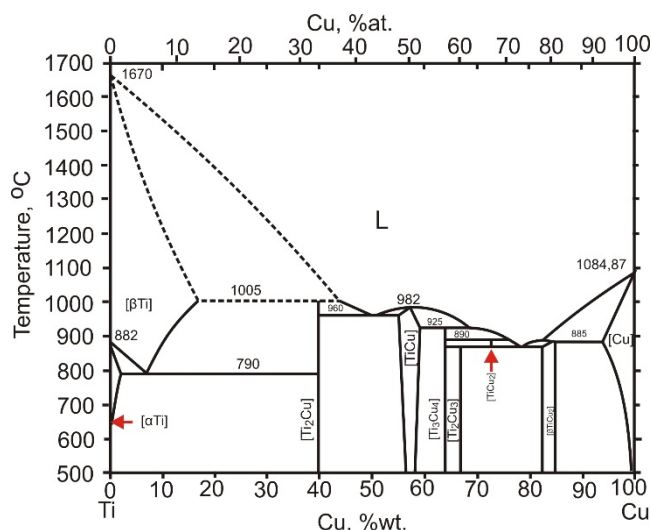


Fig. 1. Phase equilibrium diagram of Ti-Cu [8]

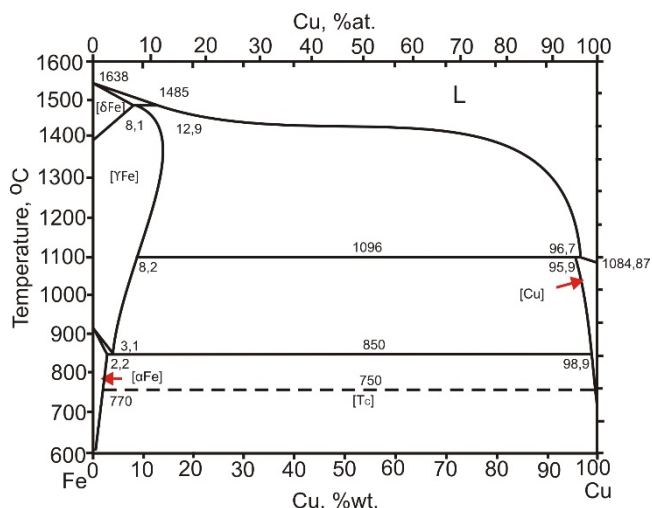


Fig. 2. Phase equilibrium diagram of Fe-Cu [8]

Iron copper – copper with small iron additives creates a very interesting and forward-looking group of materials, characterized by good performance [9]. The maximum iron solubility in copper is 4,1 wt. % at peritectic transformation temperature 1096 °C (Figure 2.) [37]. They are used to make of elastic components,

enclosures for electronic devices, telecommunications equipment and measuring apparatus and other things [7, 8].

The thermodynamic analysis of the Cu-Fe-Ti system was carried out by V. Raghavan [38]. Five three-component phases are specified in this system.

Silicon bronzes with good mechanical properties, high corrosion resistance and mechanical wear. The mechanical properties of silicon bronzes depend on the amount of silicon in the alloy. As the silicon content increases, the strength and hardness of the bronzes increases and the plasticity decreases. Silicon bronzes are widely used in the production of castings such as bushings, pump housings and valve parts, rotors, plain bearings, gears [39]. They are also popular in art foundry.

A small addition of iron has a beneficial effect on the fragmentation of the structure and increase the mechanical properties. However, when the 1.5 % Fe content is exceeded in Cu-Si-Mn-Zn-Fe and 2.5 % in Cu-Si-Fe alloys, the mechanical properties of these alloys decrease. In general, in technical alloys, the iron content is between 0.5 and 1.8 %. In silicon bronzes, microstructure fragmentation can be obtained by introducing elements with a modifying effect. The most popular and effective in the fragmentation of silicon bronze microstructure is the addition of zirconium. However, there are known examples of the use of titanium additives, which also has a deoxidizing capacity. [7, 39]. The use of the Ti73Fe complex titanium-iron master alloy in the right amount should have a positive effect on the properties of the test copper and silicon alloy.

2. Investigation methodology

The work plan involved performing tests using Ti-Fe two-component master alloy to determine the impact of titanium as the main alloy reagent when introduced into copper and copper alloy with silicon. In addition, when introducing the selected TiFe master alloy, the proportion of iron in the analysed copper and silicon bronze increased. The presence of iron is sometimes referred to as contamination and is sometimes an alloying additive that acts towards grain fragmentation in Cu alloys.

In the first stage of the study, a series of experimental casting were conducted with variable content of Ti73Fe master alloy entering copper in quantities of 0 %, 5 %, 15 %, 25 % in relation to the mass of the metal charge. Obtained specimens were named with symbols Cu, CuTi4Fe, CuTi12Fe4, CuTi19Fe7 respectively.

In the second stage, a silicon additive was introduced into copper in the amount of about 4 % by weight and 0.5 % and 1 % respectively of the initial Ti73Fe alloy. Casted specimen without the Ti73Fe addition was named CuSi4 and specimens with additions: CuSi4Ti0.4 (CuSi4 + 0.5 % Ti73Fe) and CuSi4Ti0.7 (CuSi4 + 1 % Ti73Fe).

The experimental casting was carried out in an induction furnace with a chamotte-graphite crucible. The addition of Ti73Fe master alloy was introduced at a bath temperature that vary between 1100 and 1200 °C. Finished alloys were cast into metal moulds. Samples were prepared from the obtained alloys and microstructure tests were performed, tensile strength UTS, elongation A, reduction in area RA and BHN (Brinell Hardness Number) were assessed.

During the research the following was analysed: the chemical composition of the obtained alloys according to the design of experiments, using the Spectro Midex energy dispersion X-ray fluorescence spectrometer; macro- and microstructures were investigated by the NIKON SMZ 745Z and Eclipse LV 150 microscopes (OM). Samples were ruptured by means of the INSTRON device, model 1115.

Analysis of equilibrium crystallization was performed using the CALPHAD method, using the Thermo-Calc package with the TCCU copper alloy base: TCS Cu-based Alloys Database [40, 41].

2. Results of the selected tests

Samples for the chemical composition test were taken from the casting of the metal mould. The following chemical compositions of alloys summarised in Table 1 and Table 2 were obtained as a result of the tests. In the rest of the article, alloys are identified in terms of copper, titanium and iron and silicon content (column "Type of alloy").

Table 1.

Results of the chemical composition analysis of alloy Cu+Ti73Fe

No.	Type of alloy	Cu	Ti	Fe	Mo	Mn	Zn	Rest
1	Cu	99.26	0.03	0.03	0.30	0.03	0.33	0.02
2	CuTi4Fe	94.15	3.74	1.38	0.30	0.15	0.15	0.13
3	CuTi12Fe4	83.60	11.55	4.30	0.30	0.03	0.20	0.02
4	CuTi19Fe7	73.78	18.84	6.93	0.30	0.03	0.19	0.01

Table 2.

Results of the chemical composition analysis of alloy CuSi4+Ti73Fe

No.	Type of alloy	Cu	Si	Ti	Fe	Mo	Zn	Rest
5	CuSi4	95.17	4.12	0.03	0.03	0.31	0.33	0.01
6	CuSi4Ti0.4	94.78	4.10	0.37	0.13	0.28	0.31	0.03
7	CuSi4Ti0.7	94.36	4.07	0.73	0.27	0.26	0.29	0.02

Figures 3-6 show examples of characteristic images of microstructures from the first stage of testing, i.e. the assessment of the impact of variable additions of TiFe master alloy for electrolytic copper M1E.

The microstructure of pure copper used for the test process shows the dendritic structure, a bright copper solution (Cu) is visible with the separations at the boundaries of the Cu-Cu₂O aerobic eutectic grains.

The introduction of the Ti73Fe master alloy additive globally changes the microstructure of the test alloy. The master alloy has a strong deoxidizing effect. In the microstructure, the disappearance of Cu-Cu₂O eutectic is noticeable (Figures 4-6).

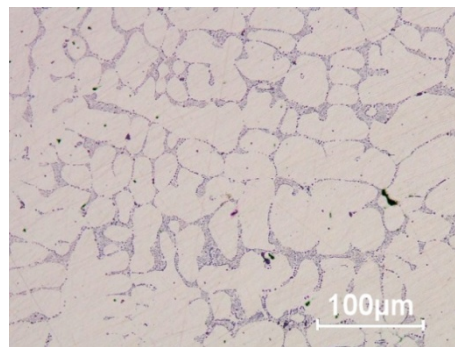


Fig. 3. Microstructure image of Cu, 200x

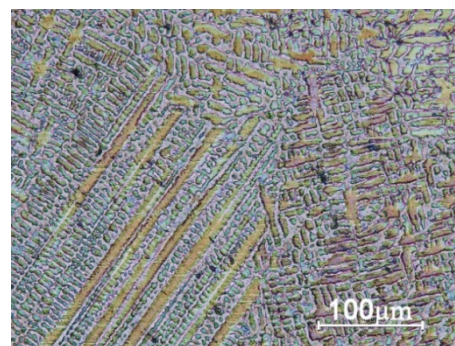


Fig. 4. Microstructure image of CuTi4Fe, 200x

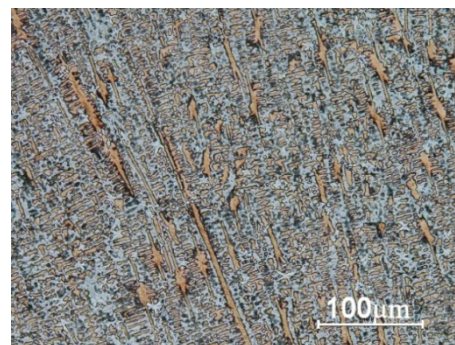


Fig. 5. Microstructure image of CuTi12Fe4, 200x

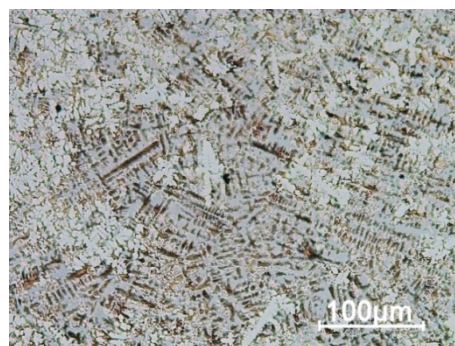


Fig. 6. Microstructure image of CuTi19Fe7, 200x

In the next stage, the CuSi4 two-component silicon bronze was introduced with a Ti-Fe master alloy in different quantities. Figures 7-9 show the microstructures of the experiment.

The CuSi4 output alloy microstructure after casting exhibits a dendritic structure - two-phase. Dendrites are formed from the α phase, and interdendrital spaces have phase γ euctinics.

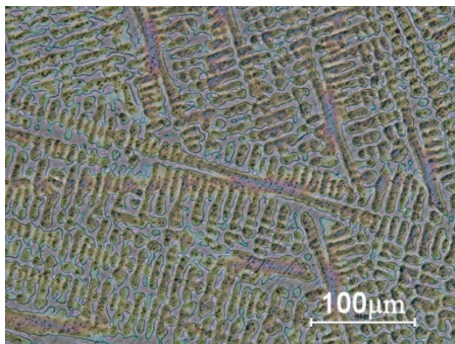


Fig. 7. Microstructure image of CuSi4, 200x

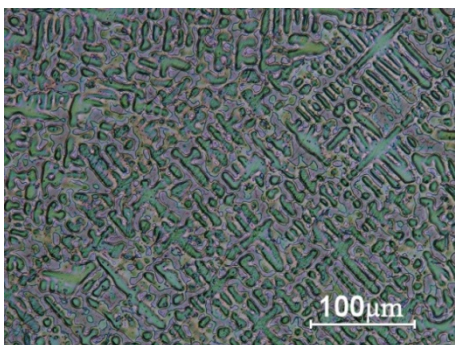


Fig. 8. Microstructure image of CuSi4Ti0.4, 200x

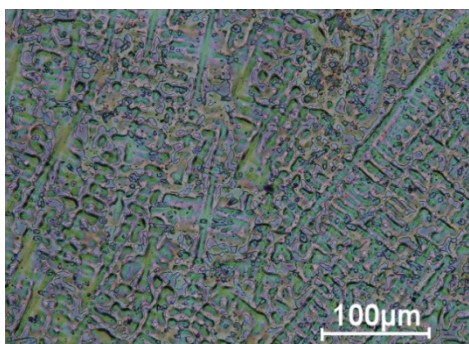


Fig. 9. Microstructure image of CuSi4Ti0.7, 200x

The resulting images of microstructures from stages one and two showed, after initial analysis, a clear effect of the additive used in both pure copper and silicon bronze. The changes are mainly related to the crystallization process in the grain area, but the morphology of detected dendrites also changes.

Visible changes in the microstructure, as a rule, cause changes in mechanical properties. The results of the tests of the obtained properties of both experiments are shown in Table 3. Individual properties are shown graphically in Figure 10 and 11.

Table 3.

Results of testing mechanical properties of samples from individual experiments

Type of alloy	UTS	Elongation A	RA	BHN
	[MPa]	%	%	-
Cu	88	9.5	4.9	32
CuTi4Fe	352	8.2	7.3	151
CuTi12Fe4	412	0.8	1.0	290
CuTi19Fe7	155	0.3	0.4	400
CuSi4	215	4.5	4.9	134
CuSi4Ti0.4	320	9.1	1.9	126
CuSi4Ti0.7	119	4.6	1.4	120

The results of the strength properties confirm the beneficial effect of titanium and iron introduced in the form of the Ti73Fe pre-alloy. The applied additive significantly increased the hardness and tensile strength of the alloy. The maximum strength was achieved with 15 % of the master alloy additive, which represented 11.55 % and 4.3 % of the Ti and Fe content of the alloy (CuTi12Fe4). However, the lower titanium and iron content of 3.7 % and 1.3 % (CuTi4Fe) in the alloy, respectively, makes the resulting material more favourable.

The properties of the CuSi4 silicon copper are improved after the addition of 0.5 % Ti73Fe master alloy, representing 0.4 % titanium and 0.1 % iron alloy content (CuSi4Ti0.4). A larger addition of titanium has resulted in a deterioration of all the strength properties of the alloy. The observed dependencies are shown in Figures 10 and 11.

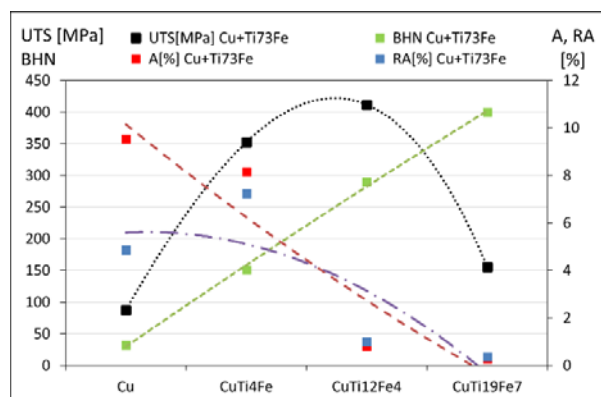


Fig. 10. Graphical listing of the mechanical properties results of samples from individual experiments Cu+Ti73Fe

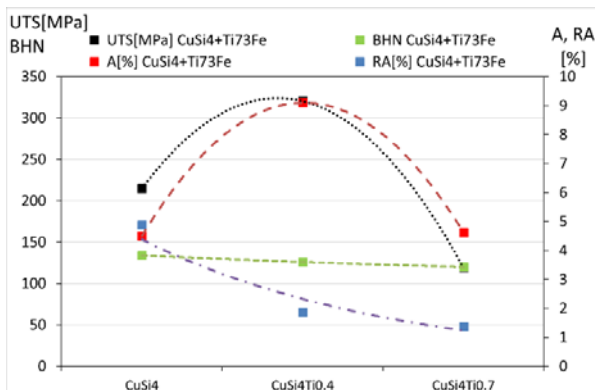


Fig. 11. Graphical listing of the mechanical properties results of samples from individual experiments CuSi4+Ti73Fe

4. CALPHAD thermodynamic modelling

The microstructure analysis was verified based on the results of CALPHAD calculations. CALPHAD alloy modelling using Thermo-Calc software was performed for alloys obtained in the experiment. A simulation of the alloy cooling process was simulated taking into account phase changes under equilibrium conditions. In addition, modelling for alloy 11 (Cu-O for oxygen content 0.5 %) was carried out. In the case of alloy 1 (Cu) with few impurities such as Ti, Fe, Mo, Mn, Zn, the presence of 0,5 % aerobic eutectic Cu-Cu₂O was observed in the microstructure, which was included in the Thermo-Calc modelling.

Modelling graphs of the theoretical crystallization of the test alloys were obtained. An example of a CuTi12Fe4 alloy cooling simulation graph is shown in Figure 12. Temperatures T1 and T2 are the temperatures at which under assumption of thermodynamic equilibrium conditions it is possible nucleation and growth of successive phases from liquid and at temperatures T3 and T4 in the solid state. At T3 temperature, we observe the end of the crystallization – no more LIQUID phase is present below this temperature. The T5 temperature can be taken as the ambient temperature.

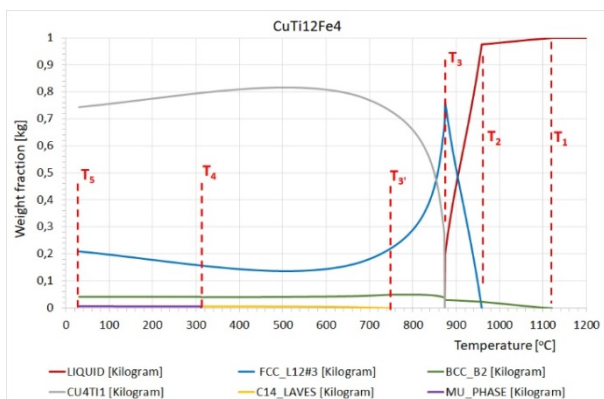


Fig. 12. Simulation of the crystallization of alloy 3 with marked characteristic transformation temperatures.

Table 4. Results of characteristic copper phase change temperatures with TiFe additives modelled using Thermo-Calc

Sample	T ₁ [°C]	T ₂ [°C]	T ₃ [°C]	T ₄ [°C]	T ₅ [°C]	Weight fraction in 30°C	Weight percent of element in phase
11 (Cu-CuO)							
LIQUID [kg]	1082	1066					
FCC_L12 [kg]		1082	1066	30	0,9955	Cu 100,00	
CUPRITE_C3 [kg]			1066	30	0,0045	Cu 88,8190 O 11,1810	
1 (Cu)							
LIQUID [kg]	1230	1062					
FCC_L12 [kg]		1080	1066	30	0,9903	Cu 99,6673 Zn 0,3025 Mn 0,0298	
CUPRITE_C3 [kg]			1063	30	0,0045	Cu 88,8190 O 11,1810	
BCC_B2 [kg]		1230		30	0,0026	Mo 99,7942 Mn 0,2056 Ti 0,0002	
CU4TI1 [kg]				276	0,0019	Cu 84,4781 Ti 15,5219	
MU_PHASE [kg]				530	0,0007	Mo 59,5515 Fe 40,4039	
2 (CuTiFe)							
LIQUID [kg]	1185	952					
FCC_L12 [kg]		1044	786	30	0,7423	Cu 99,5970 Zn 0,20208 Mn 0,2009 Ti 0,00002	
C14_LAVES [kg]			771	311			
BCC_B2 [kg]		1085	923				
BCC_B#3 [kg]			815	30	0,0118	Fe 99,9226 Mo 0,0770 Mo 0,0004	
CU4TI1 [kg]			786	30	0,2409	Cu 84,4766 Ti 15,5234	
MU_PHASE [kg]		1051-1038	955-771	311-30	0,0050	Mo 59,5522 Fe 40,4237 Cu 0,0241	
3 (CuTi12Fe4)							
LIQUID [kg]	1120	872					
FCC_L12 [kg]		958	872	30	0,2103	Cu 98,9177 Zn 0,9508 Mn 0,1315 Ti 0,00013	
C14_LAVES [kg]			746	311			
BCC_B2 [kg]		1120	872	30	0,0410	Fe 99,9426 Mo 0,00038 Mn 0,057	
CU4TI1 [kg]			872	30	0,7436	Cu 84,4680 Ti 15,5320	
MU_PHASE [kg]			872	311	0,0050	Mo 59,5522 Fe 40,4238 Cu 0,0239	
4 (CuTi19Fe7)							
LIQUID [kg]	1130	850					
FCC_L12 [kg]		850	30	0,0069		Cu 75,1659 Zn 34,8171 Mn 0,0168 Ti 0,00024	
C14_LAVES [kg]			665	316			
BCC_B2 [kg]		1130	873/862	30	0,0674	Fe 99,7974 Mo 0,00039 Mn 0,2015 Ti 0,00068	
CU4TI1 [kg]			873	30	0,6779	Cu 84,1568 Ti 15,8432	
CU3TI2 [kg]			862	30	0,2423	Cu 66,5640 Fe 33,4360	
MU_PHASE [kg]				316	0,0050	Mo 59,5532 Fe 40,4359 Cu 0,0109	
CUMNZN [kg]				59	0,0005	Cu 34,6293 Zn 35,522 Mn 29,849	

Crystallizing pure copper should solidify at a constant temperature of 1084.84 °C (TC 1082 °C – FCC_L12). Small amount of dissolved oxygen in copper (0.5 %) will cause the appearance at 1066 °C of the so-called aerobic CUPRITE_C3 eutectic.

Introducing titanium together with iron in the Ti73Fe master alloy into copper: titanium mainly secretes in phases with Cu₄Ti and Cu₃Ti₂ copper, and iron mainly for BCC_B2, BCC_B#3 and MU_PHASE. The FCC_L12 phase is mainly copper and small separation of other alloying components, a similar situation occurs in phases of type BCC. The exact compositions of each phase are shown in Table 4.

The results of the participation of the individual phases at 30 °C are graphically presented (Figure 13).

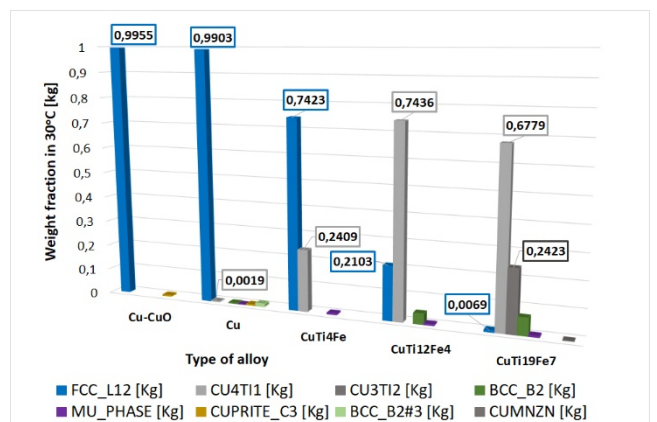


Fig. 13. Weight fraction of copper phases with TiFe additives at 30 °C modelled using Thermo-Calc

Modelling for CuSi4 alloy is as follows (Table 5): at ambient temperature, the main structural components are FCC_L12 solution (Cu 97.6 wt. %, Si 1.9 wt. %, Zn 0.4 wt. %) and phase Cu₅₆Si₁₁_GAMMA (with a composition of Cu_{91.9}Si_{7.9}Zn_{0.1}). A small addition of titanium induces an increasing phase share of Cu₄Ti (Cu_{84.4}Ti_{15.6}) and iron-phase FeSi₂_L. Graphically, the mass participation of phases modelled with the Thermo-Calc CuSi4 alloy program with TiFe additives at 30 °C is shown in Figure 14.

Table 5. Results of characteristic phase transformation temperatures of CuSi4 alloy modelled using Thermo-Calc

Sample	T ₁ [°C]	T ₂ [°C]	T ₃ [°C]	T ₄ [°C]	T ₅ [°C]	Weight fraction in 30°C	Weight percent of element in phase
5 (CuSi4)							
LIQUID [Kg]	1227	984	906			0,6370	Cu 97,6142 Si 1,9387 Zn 0,4471 Ti 0,00002
FCC_L12 [Kg]		984		470	30	0,0031	Mo 99,9997 Ti 0,0003
BCC_B2 [Kg]	1227					0,3574	Cu 91,8859 Si 7,9877 Zn 0,1264
CU56SI11_GAMMA [Kg]				470	30	0,0019	Cu 84,3783 Ti 15,6215
CU4TI1 [Kg]			791	276			
FE_S12 [Kg]				155	30	0,0006	Si 50,1442 Fe 49,8558
FE_S12_L [Kg]							
6 (CuSi4Ti0.4)							
LIQUID [Kg]	1205		893			0,6259	Cu 97,6328 Si 1,9387 Zn 0,4285 Ti 0,00002
FCC_L12 [Kg]		980	893		30	0,0028	Mo 99,9997 Ti 0,0003
BCC_B2 [Kg]	1205					0,3450	Cu 91,8911 Si 7,9877 Zn 0,1212
CU56SI11_GAMMA [Kg]				448	30	0,0237	Cu 84,3783 Ti 15,6215
CU4TI1 [Kg]				440	30		
FE_S12 [Kg]		911		155			
FE_S12_L [Kg]						0,0026	Si 50,1442 Fe 49,8558
7 (CuSi4Ti0.7)							
LIQUID [Kg]	1188	975	882			0,6203	Cu 97,6541 Si 1,9387 Zn 0,4072 Ti 0,00002
FCC_L12 [Kg]		975			30	0,0026	Mo 99,9997 Ti 0,0003
BCC_B2 [Kg]	1188					0,3250	Cu 91,8971 Si 7,9877 Zn 0,1152
CU56SI11_GAMMA [Kg]				447	30	0,0467	Cu 84,3783 Ti 15,6215
CU4TI1 [Kg]				405	30		
FE_S12 [Kg]		953		155		0,0054	Si 50,1442 Fe 49,8558
FE_S12_L [Kg]							
CU3TI2 [Kg]				518	458		

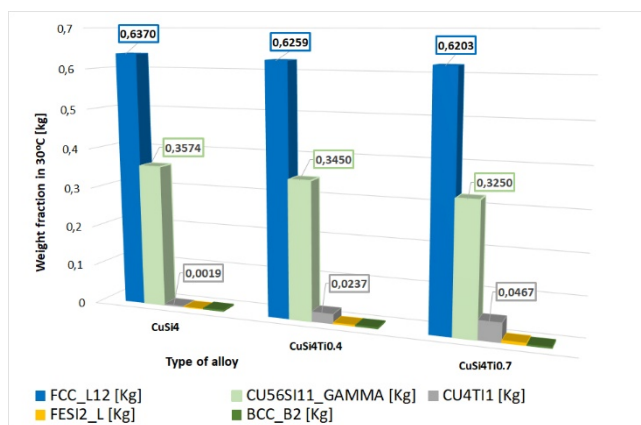


Fig. 14. Weight fraction of CuSi4 alloy phases with TiFe additives at 30 °C modelled using Thermo-Calc

5. Conclusions

The CALPHAD method simulates the cooling and crystallization processes of the test alloys. This allows you to identify the phases responsible for the individual properties of the test alloys. The experimental process of the experiment, i.e. images of microstructures and the resulting characteristics of strength properties gain additional confirmation by determining the theoretical participation of the individual structural

components. The tool in the form of Thermo-Calc software allows to obtain detailed data, obtained experimentally only by means of phase identification by analytical methods (XRD, SEM-EDS, EBSD).

Analyzing the effects of titanium together with the iron introduced into pure copper, we observe the following changes. The FCC_L12 phase practically reads copper is characterized by relatively small properties. The introduction of the Ti73Fe triggered the appearance of Cu₃Ti₂ phase hard separations in the microstructure (Ti value at a rate above 11.55 %) which caused a sharp increase in hardness, at the expense of a decrease in the strength of the alloy – a visible degradation of the beneficial microstructure. Titanium in the amount of 3.7 and 11.55 % has a positive effect in copper, causing crystallization of the Cu₄Ti phase in the amount of 0.2 and 0.7 % respectively at the expense of depletion of the FCC_L12. This results in a high tensile strength alloy with suitably high plasticity or high hardness. The impact of Ti and Fe was graphically demonstrated in the form of a mass phase share combination with selected properties of UTS, BHN for subsequent copper alloys: CuTi4Fe, CuTi12Fe4, CuTi19Fe7 (Figure 15).

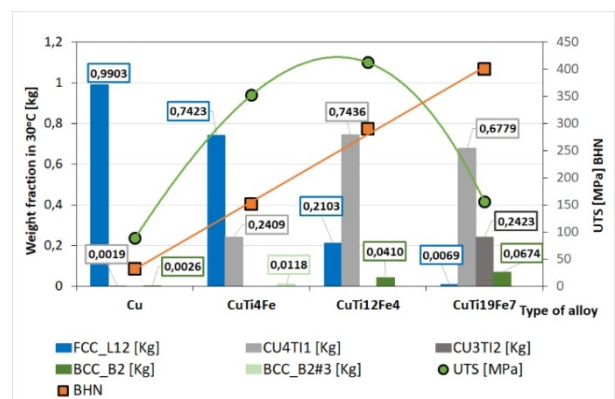


Fig. 15. Weight fraction of phases with selected copper properties (UTS, BHN) with TiFe additives (UTS, BHN)

The tests carried out on CuSi4 allow the following conclusions to be obtained. Introducing titanium and iron in the Ti73Fe master alloy, the main impact is evident through the appearance of the Cu₄Ti phase. The addition of titanium in the amount of 0.4 % resulted in the separation of the Cu₄Ti phase in the amount of 0.02 %, causing the desired formation of the components of the microstructure, which resulted in an increase in tensile strength and plasticity with a slight decrease in the hardness of the alloy. Above this value, beneficial separations of structural components are degraded, resulting in a decrease in the mechanical properties of CuSi4. The influence of Ti and Fe in copper with silicon is shown graphically in the form of a juxtaposition of phase mass participation with selected properties of UTS, BHN for subsequent copper alloys: CuSi4, CuSi4Ti0.4, CuSi4Ti0.7 (Figure 16).

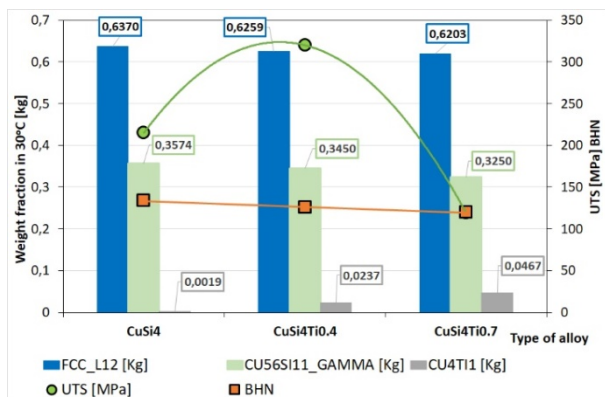


Fig. 16. Weight phase share with selected CuSi4 alloy properties (UTS, BHN)

The metallographic tests carried out and the results obtained from selected mechanical properties of the analysed alloys demonstrated the validity of the studies undertaken. Changes were achieved in the microstructure, mainly within the grain, but also in the developed dendrites of the solid solution. Changes occur with the introduction of titanium with iron into copper as well as to two-component silicon bronze.

The pre-alloy used showed a favourable performance, both in terms of master alloy solubility and in the area of improvement of strength properties. Experiments confirmed the validity of the use of Ti73Fe master alloy as an additive. Titanium in this form is easily introduced into pure copper as well as copper alloy with silicon causing changes in the properties of the test alloys.

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