

The Effect of Aluminium Amount on the Combustion Temperature and Microstructure of Ti-Al alloy After Reactive Sintering

Andrea Školáková, Pavel Salvetr, Pavel Novák

University of Chemistry and Technology in Prague, Department of Metals and Corrosion Engineering, Technická 5, 166 28 Prague 6, Czech Republic, E-mail: skolakoa@vscht.cz, salvetrp@vscht.cz, panovak@vscht.cz

Titanium aluminides with various amounts of aluminium were prepared by Self-propagating High-temperature Synthesis (SHS). Ti-20 wt. % Al, Ti-38 wt. % Al and Ti-63 wt. % Al were chosen according to Ti-Al phase diagram, because these chemical compositions represent Ti_3Al , $TiAl$ and $TiAl_3$ phase, respectively. The effect of the amount of aluminium on the combustion temperatures, microstructure and phase composition was studied. Heating of compressed samples was observed by optical pyrometer to determine exothermic reaction which is associated with SHS reaction. It was found that reaction temperatures increased with increasing addition of aluminium as well as reaction time and the start of ignition. The expected dominant phases were determined in all systems after SHS reaction. However, other phases accompanied their formation. The largest variety of phases formed in Ti-38 wt. % Al system.

Keywords: Ti-Al alloy, combustion temperature, Self-propagating High-temperature Synthesis

1 Introduction

High temperature components, such as engine parts of airplanes or turbines, are usually made of nickel or superalloys, heat-resistant steels or even cobalt superalloys. Their main disadvantages are high density and also the fact that they are usually contain critical raw material, such as chromium, cobalt, niobium and tungsten. For this reason, new materials have been found to replace them. Titanium aluminides are promising materials for high-temperature and lightweight applications [1]. Possible applications can be found in automotive and aircraft industry such exhaust valves, jet engines, stationary turbines or space vehicles [1, 2]. However, their wider application is limited because of their very low ductility at room temperature [3]. These high-melting alloys are usually produced by melt-metallurgy which includes multistage process – melting, casting into a mold and isothermal annealing [3, 4]. However, as it was mentioned before, melting points of these intermetallics are high which is considerably inconvenient. For this reason, new methods of their production have been found. An alternative route how to fabricate high-melting metals is powder metallurgy, especially reactive sintering [5, 6, 7, 8].

High-melting intermetallics are usually prepared by combustion synthesis which involves SHS reaction. Self-propagating High-temperature (SHS) also called reactive sintering can be divided into two modes. First involves Thermal Explosion mode in which reaction is initiated by heating of whole mixture. Second mode is called Plane Wave propagation mode and reaction is initiated by heating of only one side of compressed mixture. Thermal Explosion mode is the most used method in sintering of intermetallics. Reactive sintering is a process where the initial components are metallic powders and thus, it is avoided to melting of high-melting intermetallics. These powders are heated and chemical reactions are thermally activated during heating which leads to the compaction. These reactions are strongly exothermal and they allow propagate reactions through the whole heated material.

Many works tried to describe SHS reaction in Ti-Al system [9, 10, 11]. Nowadays, it has been found that reaction between aluminium and titanium is initiated by melting of aluminium [12]. First phase which forms after the reaching of melting point of aluminium is $TiAl_3$ phase. Other phases $TiAl$ and Ti_3Al form with proceeding reaction [9]. The reason, why $TiAl_3$ phase forms first can be explained by thermodynamic and kinetic aspects of formation [11], by its value of minimum free energy [13] and activation energy which is $483 \text{ kJ}\cdot\text{mol}^{-1}$ [14]. Thus, the SHS reaction is associated with the formation of this phase. In work [15], it was found that formation of $TiAl_3$ is controlled by the rate of chemical reaction at the temperature of 800°C . However, another work [10] claimed that the formation of this phase is associated with the diffusion [11] when temperature is lower than 660°C . Thus, temperature affects the mechanism of phase formation. Other parameters of reaction play an important role in intermediary phase formation. It is mainly the effect of heating rate [16]. Ignition temperature of combustion decreases with increasing heating rate. Moreover, low heating rate leads to the liquid aluminium and solid titanium reaction mechanism whereas high heating rate leads to the solid-solid reaction mechanism [16]. However, studies have focused on Ti-Al system with excess of aluminium for example Ti-75 at. % Al [9, 10, 17]. The other important parameters playing significant role in thermodynamic analysis of combustion and ignition temperatures are stoichiometry and reactant particle size [16]. These temperatures are used in calculations of reactions enthalpy, being applied for the optimization of the heating/cooling demands of the SHS technology

For this reason, the effect of amount of aluminium was studied in Ti-Al system. The combustion temperature, the ignition temperature and temperature of the end of reaction were observed. Further, the amount of aluminium on microstructure and phase composition was also studied. Samples were prepared by Self-propagating High-temperature Synthesis mode with fast heating localized on one side of sample.

2 Experimental

Samples Ti-20Al, Ti-38Al and Ti-63Al (in wt. %) were prepared by mixing of pure powders of titanium (purity 99.5 %, particle size 44 μm) and aluminium (purity 99.62, particle size 44 μm). This mixture was subsequently cold pressed by the means of LabTest5.250SP1-VM universal loading machine at a pressure of 450 MPa for 5 minutes. Cylindrical green bodies with the diameter of 10 mm were obtained. Compressed powders were inserted into induction furnace and heated under Ar atmosphere with heating rate approximately $90\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$. Heating of samples was recorded by optical pyrometer Optris OPTP20 – 2M which enabled to observe the course and temperature profile of SHS reaction. Temperature as a function of time during heating was obtained.

All samples were ground by sandpapers with SiC abrasive particles (P80 – P4000) after measurement of SHS reactions. Suspension of colloidal silica Eposil F with hydrogen peroxide (volume 1:6) were used to polish the samples and Kroll's reagent (5 ml HNO_3 , 10 ml HF, 85 ml H_2O) was applied in order to reveal the microstructure features by etching. Microstructure was observed by TESCAN VEGA 3 LMU scanning electron microscope equipped with Oxford Instruments X-max 20 mm² SDD EDS analyzer to determine the chemical composition. Phase composition was determined by X-ray diffraction and evaluated using PANalytical X'Pert Pro software package with PDF2 database.

3 Results

Three systems were studied in this article: Ti:Al=3:1, Ti:Al=1:1 and Ti:Al=1:3. Fig. 1 shows the temperature-time plot for TiAl20, TiAl38 and TiAl63 (in wt. %) compressed powder mixtures. As it can be seen, the ignition of the reaction depends on the amount of aluminium. Initiation (start) temperature of the ignition increases with increasing of the aluminium weight fraction in powder mixture. Ignition of the reaction was observed 187 s for TiAl20, 231 s for TiAl38 and 240 s for TiAl63 system after the start of the heating. The transformation to the final product was completed shortly (approximately 33 s) and reaction time increased with increasing the amount of aluminium. That means very rapid SHS reaction between powders aluminium and titanium. Exothermic peaks observed during heating are associated with the heat release and the formation of Ti-Al intermetallic phases. The phase composition of the SHS products is presented below. No endothermic peak or plateau corresponding to Al melting was observed. For this reason, heating rate was too high and melting of aluminium was impossible to detect. However, it has been known that reaction is not initiated until the temperature reaches the melting point of aluminium [15]. When we compare the shape of exothermic peaks, it is clear that the amount of aluminium of 38 wt. % causes the highest exothermicity of reaction.

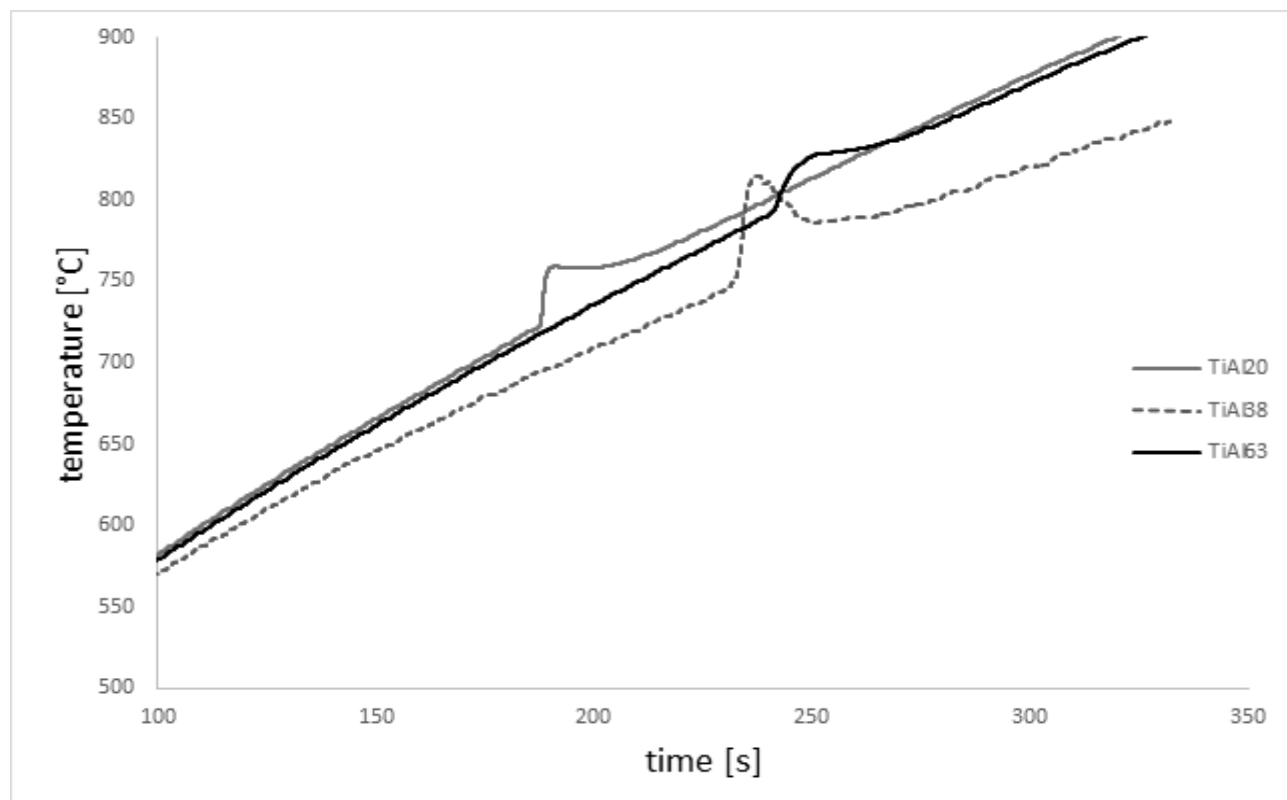


Fig. 1 Heating curves of Ti-Al powder mixture recorded by optical pyrometer

Reaction temperatures were determined according to heating curves and they are shown in Tab. 1. T_{onset} is the temperature of beginning of reaction, T_{maximum} is also

called combustion temperature and T_{offset} is the temperature of the end of reaction. The amount of aluminium increases T_{onset} and suggesting that its amount moves start

of reaction to higher temperatures. All temperatures of reaction start are higher than the melting point of aluminium. It indicates that liquid aluminium reacts with solid titanium. The highest combustion temperature was found in TiAl63 system and thus, aluminium increases T_{maximum} of reaction. However, combustion temperatures did not

exceed the adiabatic temperatures which are usually higher than 1200 °C for all Ti-Al systems. It is the maximum temperature which could be achieved during SHS reaction [18]. Higher addition of aluminium also increases T_{offset} .

Tab. 1 Reaction temperatures of Ti-Al alloys

| Alloys | T_{onset} [°C] | T_{maximum} [°C] | T_{offset} [°C] |
|--------|-------------------------|---------------------------|--------------------------|
| TiAl20 | 719 | 759 | 763 |
| TiAl38 | 745 | 811 | 799 |
| TiAl63 | 791 | 827 | 840 |

Resulted microstructure of sintered TiAl20 alloy is shown in Fig. 2 and phase composition is summarized in Table 2. It can be seen that there are still unreacted particles of titanium. These unreacted particles are surrounded by Ti_3Al and TiAl phases. So, both phases nucleated and grew towards the original Ti particle. These phases formed preferentially, because this system contained of excess of titanium. For this reason, solid titanium and liquid aluminium reacted mutually and phases enriched by titanium could form at the interface as reaction proceeds. XRD analysis confirmed phases which were found during local chemical analysis (Tab. 2). It can be assumed that the main phase forming during SHS reaction is Ti_3Al phase which belongs to the group of ordered intermetallic compounds with ordered hexagonal close-packed superlattice structure [19].

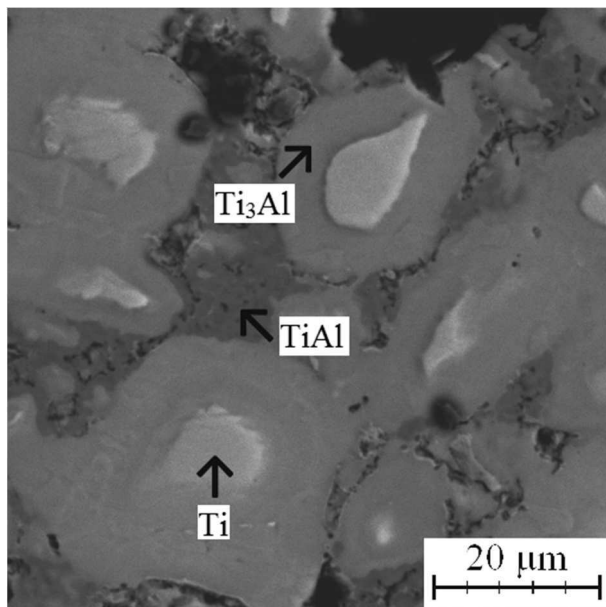


Fig. 2 Microstructure of TiAl20 (in wt. %) alloy

Microstructure of TiAl38 alloy is mainly formed by Ti_3Al phase surrounded by TiAl phase and then TiAl_2 phase (Fig. 3). TiAl phase was also dispersed in TiAl_2 phase. These two areas contained of TiAl phase with ordered face-centered cubic based superlattice structure [19] and for this reason, this phase probably formed during SHS reaction. Moreover, phases found in our system are phases locating around TiAl phase according to diagram Ti-Al [20] and TiAl phase created coexisting phases

with them. XRD analysis also revealed other phases - Ti_2Al_5 and TiAl_3 (Tab. 2). Higher addition of aluminium caused that unreacted titanium was not detected and phases enriched by aluminium formed (Tab. 2). Final product consisted of the most phases from all of the studied samples (Table 2).

Tab. 2 Phase composition of Ti-Al alloys

| Alloys | Phase composition |
|--------|---|
| TiAl20 | Ti, Ti_3Al , TiAl |
| TiAl38 | Ti_3Al , TiAl, TiAl_2 , Ti_2Al_5 , TiAl_3 |
| TiAl63 | TiAl_2 , Ti_2Al_5 , TiAl_3 |

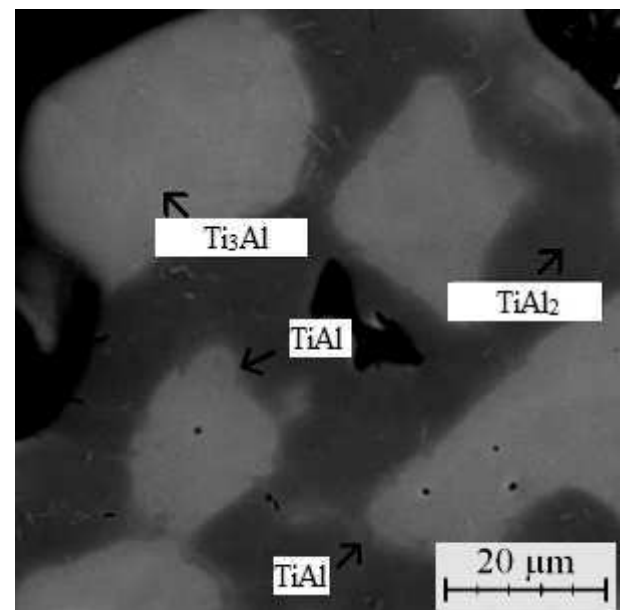


Fig. 3 Microstructure of TiAl38 (in wt. %) alloy

Fig. 4 shows microstructure of sintered TiAl63 alloy. TiAl_3 phase was found together with TiAl_2 where this one was dispersed or was present around TiAl_2 . Thus, TiAl_3 phase forms during SHS reaction. This explains higher temperatures during heating (Tab. 1). It was found that heat associated with the formation of TiAl_3 phase increases the temperatures [11]. Further, Ti_2Al_5 phase was also detected by XRD analysis (Table 2). Reaction between titanium and aluminium leads to the formation of TiAl_2 and TiAl_3 . Because this system contained of the excess of aluminium, phases enriched by aluminium were found the most and formed preferentially. Chemical composition corresponds to TiAl_3 phase however it was found

that there are places with TiAl_3 phase containing of over 70 wt. % of aluminium. This chemical composition corresponds to area TiAl_3+Al in diagram Ti-Al [20]. TiAl_3 phase has the same structure as in the case of TiAl phase [19].

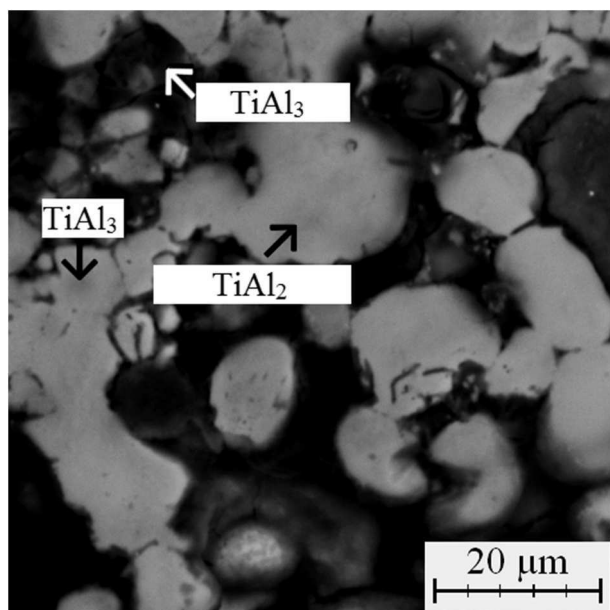


Fig. 4 Microstructure of TiAl_{63} (in wt. %) alloy

4 Conclusion

In this work, the effect of the amount of aluminium on the reaction temperatures, microstructure and phase composition was studied. It was found that the start temperature of reaction as well as reaction time increased with increasing the addition of aluminium. Combustion temperature and the end of reaction also increased with higher amount of aluminium. The study of microstructure and phase composition revealed, which phase formed during SHS reaction. Ti_3Al , TiAl and TiAl_3 phases form in TiAl_{20} , TiAl_{38} and TiAl_{63} system, respectively. However, other phases accompanied the formation of these main phases.

Acknowledgement

This research was financially supported by Czech Science Foundation, project P108/12/G043 and by specific university research (MSMT No 21-SVV/2018).

References

- [1] HASHIMOTO, K., KIMURA, M., SUYAMA, R. (1994). Alloy design of gamma titanium aluminide intermetallic compounds. In: *Nippon Steel Technical Report*, No. 62, pp. 98 – 103. Nippon Steel & Sumitomo Metal. Japan.
- [2] LAGOS, M. A., AGOTE, I., SAN JUAN, J. M., HENNICKE, J. (2014). Fabrication of TiAl alloys by alternative powder methods. In: *Gamma Titanium Aluminide Alloys 2014: A Collection of Research on Innovation and Commercialization of*

Gamma Alloy Technology, pp. 77 – 82. Wiley Online Library. USA.

- [3] BEWLAY, B. P., NAG, S., SUZUKI, A., WEIMER, M. J. (2016). TiAl alloys in commercial aircraft engines. In: *Materials at High Temperatures*, Vol. 33, No. 4-5, pp. 549 – 559. Taylor & Francis Online. United Kingdom.
- [4] KVANIN, V. L., BALIKHINA, N. T., VADCHENKO, S. G., BOROVINSKAYA, I. P., SYCHEV, A. E. (2008). Preparation of $\gamma\text{-TiAl}$ intermetallic compounds through Self-Propagating High-Temperature Synthesis and compaction. In: *Inorganic Materials*, Vol. 44, No. 11, pp. 1327 – 1331. Springer. Germany.
- [5] ŠKOLÁKOVÁ, A., NOVÁK, P., SALVETR, P. (2016). Influence of elements with high affinity to oxygen on microstructure and phase composition of Ni-Ti alloy. In: *Manufacturing technology*, Vol. 16, No. 4, pp. 808 – 814. UJP. Czech Republic.
- [6] ŠKOLÁKOVÁ, A., NOVÁK, P., SALVETR, P. (2016). Thermal analysis of Ni-Ti-X alloys prepared by Self-propagating High-temperature Synthesis. In: *Manufacturing technology*, Vol. 16, No. 5, pp. 1146 – 1150. UJP. Czech Republic.
- [7] SALVETR, P., ŠKOLÁKOVÁ, A., NOVÁK, P. (2016). Changes in microstructure and properties of Ni-Ti alloy after addition of ternary alloying element. In: *Manufacturing technology*, Vol. 16, No. 6, pp. 1359 – 1363. UJP. Czech Republic.
- [8] SALVETR, P., DANAY, B., NOVÁK, P. (2016). Comparison of Ni-Ti-Si alloy prepared by various powder metallurgy routes. In: *Manufacturing technology*, Vol. 16, No. 5, pp. 1136 – 1140. UJP. Czech Republic.
- [9] YANG, W. Y., WEATHERLY, G. C. (1996). A study of combustion synthesis of Ti-Al intermetallic compounds. In: *Journal of Material Science*, Vol. 31, No. 14, pp. 3707 – 3713. Springer. Germany.
- [10] WANG, T., LIU, R. Y., ZHU, M. L., ZHANG, J. S. (2002). Activation energy of self-heating process studied by DSC. Combustion synthesis mixture of Ti-75 at% Al. In: *Journal of Thermal Analysis and Calorimetry*, Vol. 70, No. 2, pp. 507 – 519. Springer. Germany.
- [11] PENG, L. M., WANG, J. H., LI, H., ZHAO, J. H., HE, L. H. (2005). Synthesis and microstructural characterization of $\text{Ti-Al}_3\text{Ti}$ metal intermetallic laminate (MIL) composites. In: *Scripta Materialia*, Vol. 52, No. 3, pp. 243 – 248. Elsevier. Netherlands.
- [12] MA, Y., FAN, Q., ZHANG, J., SHI, J., XIAO, G., GU, M. (2008). Microstructural evolution during self-propagating high-temperature synthesis

- of Ti-Al system. In: *Journal of Wuhan University of technology - Materials Science Edition*, Vol. 23, No. 3, pp. 381 – 385. Springer. Germany.
- [13] SUJATA, M., BHARGAVA, S., SANGAL, S. (1997). On the formation of TiAl_3 during reaction between solid Ti and liquid Al. In: *Journal of Materials Science Letters*, Vol. 16, No. 14, pp. 1175 – 1178. Springer. Germany.
- [14] SOHN, H. Y., WANG, X. (1996). Mathematical and experimental investigation of the self-propagating high-temperature synthesis (SHS) of TiAl_3 and Ni_3Al intermetallic compounds. In: *Journal of Materials Science*, Vol. 31, No. 12, pp. 3281 – 3288. Springer. Germany.
- [15] ŠKOLÁKOVÁ, A., SALVETR, P., NOVÁK, P., NÝVLTOVÁ, M. (2017). Formation of phases in Ti-Al system at 800 °C. In: *Manufacturing Technology*, Vol. 17, No. 5, pp. 838 – 842. UJP. Czech Republic.
- [16] YI, H. C., PETRIC, A. (1992). Effect of heating rate on the combustion synthesis of Ti-Al intermetallic compounds. In: *Journal of Materials Science*, Vol. 27. No. 24, pp. 6797 – 6806. Springer. Germany.
- [17] WANG, T., LU, Y. X., ZHU, M. L., ZHANG, J. S., JI, S. J. (2002). DSC research on critical temperature in thermal explosion synthesis reaction $\text{Ti}+3\text{Al}\rightarrow\text{TiAl}_3$. In: *Journal of Thermal Analysis and Calorimetry*, Vol. 67, No. 3, pp. 605 – 611. Springer. Germany.
- [18] VARMA, A., LEBRAT, J.-P. (1992). Combustion synthesis of advanced materials. In: *Chemical Engineering Science*, Vol. 47, No. 9 – 11, pp. 2179 – 2194. Elsevier. Netherlands.
- [19] KATTNER, U. R., LIN, J.-C., CHANG, Y. A. (1992). Thermodynamic assessment and calculation of the Ti-Al system. In: *Metallurgical Transactions*, Vol. 23, No. 8, pp. 2081 – 2090. Springer. Germany.
- [20] MASSALSKI, T. B. (1990). Binary Alloy Phase Diagrams, ASM, Materials Park.

10.21062/ujep/128.2018/a/1213-2489/MT/18/3/499

Copyright © 2018. Published by Manufacturing Technology. All rights reserved.