

# INFLUENCE OF TEMPERATURE ON THE INTERACTION KINETICS BETWEEN MOLTEN ALUMINIUM ALLOY AL99.7 AND TOOL STEEL H11

## VPLIV TEMPERATURE NA KINETIKO INTERAKCIJ MED STALJENO ALUMINIJEVO ZLITINO AL99.7 IN ORODNIM JEKLOM H11

Maja Vončina\*, Aleš Nagode, Jožef Medved, Tilen Balaško

Department for Materials and Metallurgy, Faculty of Natural Sciences and Engineering, University of Ljubljana, Aškerčeva 12, 1000 Ljubljana, Slovenia

Prejem rokopisa – received: 2023-03-09; sprejem za objavo – accepted for publication: 2023-06-29

doi:10.17222/mit.2023.825

Hot-work tool steels are used in casting and hot-forming processes and are subjected to thermal, mechanical and chemical stresses that can cause damage to various parts of the tool. Therefore, knowledge of the interaction between tool steel and molten aluminium alloy is necessary to extend the life of the tool. The present work was carried out to predict the influence of temperature on the interaction kinetics between tool steel and molten aluminium. To investigate the effect of temperature on the dissolution rate of tool steel in molten aluminium and the rate of formation of interaction layers, DSC analysis was performed at two different temperatures, 670 °C and 700 °C, for 12 h. The results were corroborated and supported by a detailed microstructure analysis.

It was found that very small temperature changes, in this case 30 °C, significantly affect the kinetics of the interaction layer's formation between the tool steel H11 and molten aluminium A199.7. All test methods show a pronounced influence of the test temperature. A significantly faster dissolution was observed in the DSC curve, with the slope of the curve being larger for the specimen tested at 700 °C, which was also confirmed by measurements of the thicknesses of the interaction layers. The thickness of the composite layer was almost the same in both cases, and the temperature has no effect on this layer. The types of interaction layers do not differ from each other.

Keywords: interaction between tool steel and molten aluminium, reaction kinetics, temperature, differential scanning calorimetry

Orodna jekla za delo v vročem se uporabljajo v postopkih litja in vročega oblikovanja in so izpostavljena toplotnim, mehanskim in kemičnim obremenitvam, ki lahko povzročijo poškodbe različnih delov orodja. Zato je za podaljšanje življenjske dobe orodja potrebno poznavanje interakcije med orodnim jeklom in staljeno aluminijevo zlitino. Raziskava je bila izvedena z namenom napovedovanja vpliva temperature na kinetiko interakcije med orodnim jeklom in staljenim aluminijem. Za proučevanje vpliva temperature na hitrost raztapljanja orodnega jekla v staljenem aluminiju in hitrost tvorbe interakcijskih plasti je bila izvedena analiza DSC pri dveh različnih temperaturah, 670 °C oziroma 700 °C, 12 h. Rezultati so bili utemeljeni in podprti s podrobno analizo mikrostrukture.

Ugotovljeno je bilo, da zelo majhne spremembe temperature, v tem primeru 30 °C, pomembno vplivajo na kinetiko nastajanja interakcijskih plasti med orodnim jeklom H11 in staljenim aluminijem A199.7. Vse raziskovalne metode kažejo izrazit vpliv preskusne temperature. Bistveno hitrejšo raztapljanje smo opazili na DSC krivulji, kjer je naklon krivulje večji pri vzorcu testiranem pri 700 °C, kar so potrdile tudi meritve debelin interakcijskih plasti. Debelina kompozitne plasti je bila v obeh primerih približno enaka, na to plast temperatura nima vpliva. Vrste interakcijskih slojev se med seboj ne razlikujejo.

Ključne besede: interakcija orodnega jekla in staljenega aluminija, kinetika reakcije, temperatura, diferenčna vrstična kalorimetrija

## 1 INTRODUCTION

Hot-work tool steels are used in casting and hot-forming processes and are subjected to thermal, mechanical and chemical stresses that can cause damage to various parts of the tool. Therefore, knowledge of the interaction between the tool steel and the molten aluminium alloy is necessary to extend the life span. Applying protective coatings to the functional surfaces of tools improves the wear resistance.<sup>1,2</sup> The interaction between the molten aluminium and the tool steel can lead to material adhering to the tool, mainly through chemical reactions,

diffusion and dissolution, which occur more rapidly at higher temperatures.<sup>3-5</sup>

The Al-Fe system consists of a solid solution based on iron and six intermetallic compounds with different iron and aluminium contents, which affect the wear resistance and durability of the tool. Studies show that the interaction layer between molten aluminium and tool steel contains Al<sub>5</sub>Fe<sub>2</sub> and Al<sub>3</sub>Fe phases, with Al<sub>3</sub>Fe growing faster in the later reaction phases and partially dissolving in molten aluminium.<sup>6-8</sup> However, the reaction kinetics at the interface can cause the formation of Al<sub>5</sub>Fe<sub>2</sub> as the main component.

This article discusses how a chemical reaction occurs between aluminium and iron due to their solubility, lead-

\*Corresponding author's e-mail:  
maja.voncina@ntf.uni-lj.si

ing to the formation of intermetallic phases in certain stoichiometric ratios based on the binary phase diagram for Al-Fe.<sup>5</sup> The most frequently formed phases are  $\text{Al}_3\text{Fe}_2$  and  $\text{Al}_{13}\text{Fe}_4$ , which form a reaction layer.<sup>3</sup> Optimal wetting and diffusion are required for the formation of these phases, which result from the difference in chemical potentials between the solid tool steel and the molten aluminium.<sup>9</sup> However, to achieve the desired mechanical and physical properties of the tools, the formation of these phases must be limited or prevented.

When tool steels dissolve in molten aluminium, the dissolution is initially intense but slows down after about 250 s due to the difficult diffusion of aluminium and iron atoms through the resulting interaction layer.<sup>3,8,10</sup> The interlayer between the tool steel and the aluminium alloy consists of an intermetallic and a composite layer, and the thickness of the interaction layer is influenced by the alloying elements in the molten aluminium and the tool steel. Tool-steel alloying elements such as chromium, manganese, silicon, molybdenum, and vanadium are present in the reaction layer and reduce or prevent the formation of an intermetallic layer.<sup>7</sup> The iron content in the aluminium alloy also affects the lower layer thickness, but should not be too high to avoid deterioration of the mechanical properties. The temperature of the aluminium melt also influences the thickness of the interaction layer, with higher temperatures leading to a thicker layer.<sup>7,11,12</sup>

The present work was carried out to predict the influence of temperature on the interaction kinetics between tool steel and molten aluminium. To investigate the effect of temperature on the dissolution rate of tool steel in molten aluminium and the rate of formation of the interaction layers, a DSC analysis was performed at two different temperatures, 670 °C and 700 °C, for 12 h. The results were substantiated and supported by a detailed SEM analysis.

## 2 MATERIALS AND METHODS

The reaction kinetics between molten aluminium and tool steel were analysed using differential scanning calorimetry (STA Jupiter 449c, NETZSCH Holding, Selb, Germany), which provides information on the dissolution rate of tool steel in molten aluminium at constant temperatures of 670 °C and 700 °C. The samples for DSC analysis were machined in the shape of a cylinder with a diameter of 4.5 mm and a height of 3 mm for the aluminium alloy and a diameter of 4.5 mm and a height of 1 mm for the tool steel. The crucibles used for DSC analysis were made of corundum. An empty crucible served as the reference material. In the instrument, the heating rate of the samples was set to 20 K·min<sup>-1</sup>, they were heated to 670 °C and 700 °C and kept there for 12 h. They were then cooled at the same rate of 20 K·min<sup>-1</sup>. The experiments were performed under a protective atmosphere. After completion of the analyses,

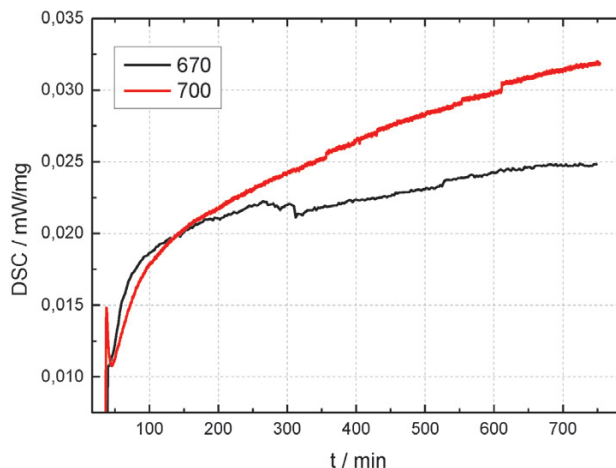
two DSC curves were plotted as a function of time, from which the effect of temperature on the reaction kinetics between the molten aluminium alloy Al99.7 and the tool steel H11 was predicted.

After completion of the DSC testing, the specimens were examined metallographically, and the thicknesses and types of interaction layers were analysed by light and scanning electron microscopy. For the microstructural characterization of the interaction layer, the specimens were carefully removed from the crucibles after the DSC analysis and placed in a horizontal position in the specimen-preparation models for the microstructural analysis to obtain an overview of the cross-section of the interaction layer between aluminium and tool steel. This was followed by metallographic specimen preparation. The specimens were then examined using an Olympus BX61 light microscope. Micrographs were produced and the thicknesses of the interaction layers were measured.

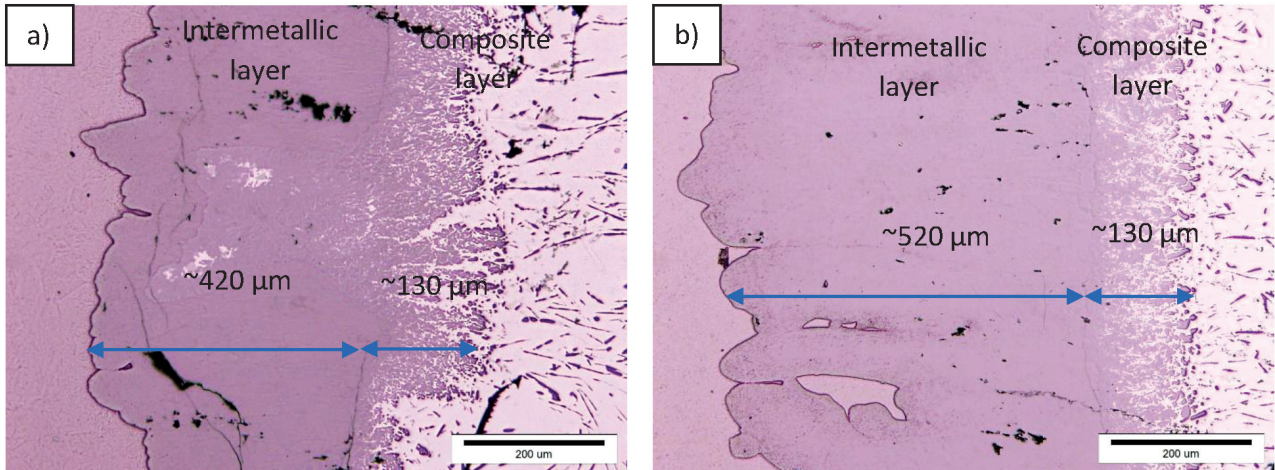
A detailed analysis of the interaction layers and the phases occurring in the interaction layer was performed using a Thermo Fisher Scientific Quattro S FEG SEM (ThermoFisher Scientific, Waltham, MA, USA) microscope with an Oxford Ultim® Max 65 mm<sup>2</sup> EDS SDD EDS analyzer (Ultim®Max, Oxford Instruments, Abingdon, UK). For imaging and EDS analyses the accelerating voltage was 15 kV. For secondary electron imaging (SEI) an Everhart–Thornley detector was used, while for the backscatter electron imaging an angular backscatter (ABS) detector was used.

## 3 RESULTS AND DISCUSSION

**Figure 1** shows the DSC curves for both samples tested at 670 °C and 700 °C. The slopes of the curves are different, with the DSC curve of the specimen tested at 700 °C rising faster and the slope being larger, indicating the faster dissolution of the tool steel in the aluminium alloy and greater diffusion of the atoms of some ele-



**Figure 1:** DSC curves of the dissolution of H11 in molten aluminium alloy Al99.7



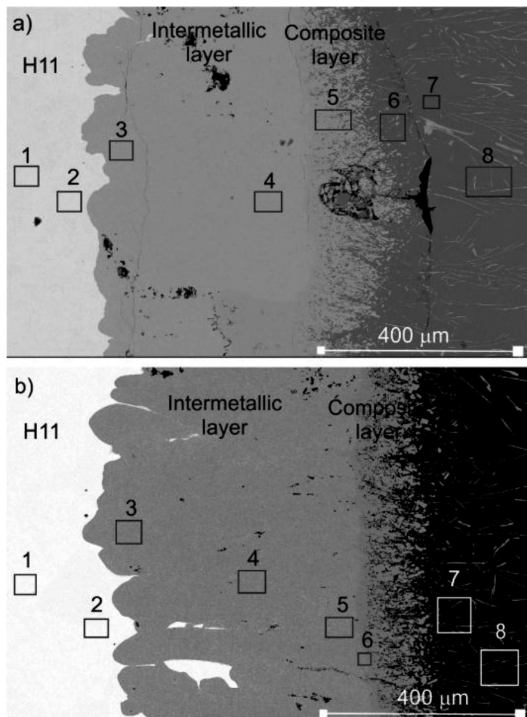
**Figure 2:** Micrographs of the interaction layers of samples tested at: a) 670 °C and b) 700 °C

ments through the protective layer. Based on these results, a thicker interaction layer is expected in the sample tested at 700 °C. The temperature difference of 30 °C plays an important role.

The microstructure analysis presented in **Figure 2** confirmed that an interaction layer was formed at the contact between the tool steel H11 and the molten aluminium Al99.7, which was divided into two parts: a layer consisting of an intermetallic phase based on  $Al_3Fe_2$  closer to the tool steel and composite layers based on the intermetallic phase  $Al_3Fe$  formed closer to the aluminium alloy.<sup>11,12</sup> As a result of the reaction between the tool steel and the liquid aluminium alloy, an  $Al_3Fe$  inter-

metallic phase is formed, which slows down the inter-phase reaction because it acts as a diffusion barrier. This is reflected in a drop in the slope of the DSC curve. The thicknesses of the layers are different. The layer closer to the tool steel has an average thickness of about 420 μm for the sample tested at 670 °C and 540 μm for the sample tested at 700 °C. The reason for the change in the thickness of the interaction layer is the faster diffusion of atoms at a higher temperature. The layer closer to the aluminium alloy is much thinner, about 130 μm in both cases.

SEM and EDS analyses confirmed that the layer closer to the tool steel consists of an intermetallic phase



| Site           | 1    | 2    | 3          | 4          | 5        | 6                    | 7           | 8                    |
|----------------|------|------|------------|------------|----------|----------------------|-------------|----------------------|
| Al             |      |      | 69.7       | 71.8       | 78.8     | 98.5                 | 99.7        | 98.4                 |
| Si             | 2.1  | 2.3  | 1.2        | 0.8        | 0.3      |                      |             | 0.3                  |
| V              | 0.3  | 0.4  | 0.1        | 0.2        |          |                      |             |                      |
| Cr             | 6.0  | 5.7  | 1.6        | 1.8        | 0.7      |                      |             |                      |
| Mn             | 0.2  | 0.3  |            |            |          |                      |             |                      |
| Fe             | 90.7 | 90.7 | 27.2       | 25.3       | 20.2     | 1.5                  | 0.3         | 1.4                  |
| Mo             | 0.7  | 0.7  | 0.2        | 0.1        |          |                      |             |                      |
| Presumed phase | H11  | H11  | $Al_3Fe_2$ | $Al_3Fe_2$ | $Al_3Fe$ | $\alpha-Al + Al_3Fe$ | $\alpha-Al$ | $\alpha-Al + Al_3Fe$ |

| Site           | 1    | 2    | 3          | 4          | 5          | 6        | 7                    | 8                    |
|----------------|------|------|------------|------------|------------|----------|----------------------|----------------------|
| Al             |      |      | 70.1       | 71.2       | 72.0       | 76.7     | 98.3                 | 98.2                 |
| Si             | 2.3  | 2.1  | 1.2        | 0.9        | 0.5        | 0.3      | 0.1                  |                      |
| V              | 0.4  | 0.3  |            |            |            |          |                      |                      |
| Cr             | 6.0  | 6.0  | 1.7        | 1.6        | 1.6        | 0.6      | 0.1                  | 0.1                  |
| Mn             | 0.6  | 0.4  | 0.1        | 0.2        | 0.2        | 0.1      |                      |                      |
| Fe             | 89.8 | 90.5 | 26.7       | 26.0       | 25.5       | 22.2     | 1.5                  | 1.7                  |
| Mo             | 0.9  | 0.7  | 0.2        | 0.1        | 0.2        | 0.1      |                      |                      |
| Presumed phase | H11  | H11  | $Al_3Fe_2$ | $Al_3Fe_2$ | $Al_3Fe_2$ | $Al_3Fe$ | $\alpha-Al + Al_3Fe$ | $\alpha-Al + Al_3Fe$ |

**Figure 3:** SEM (BEI) micrographs of the interaction layer of samples tested at: a) 670 °C and b) 700 °C. The corresponding EDS results are given in at %.

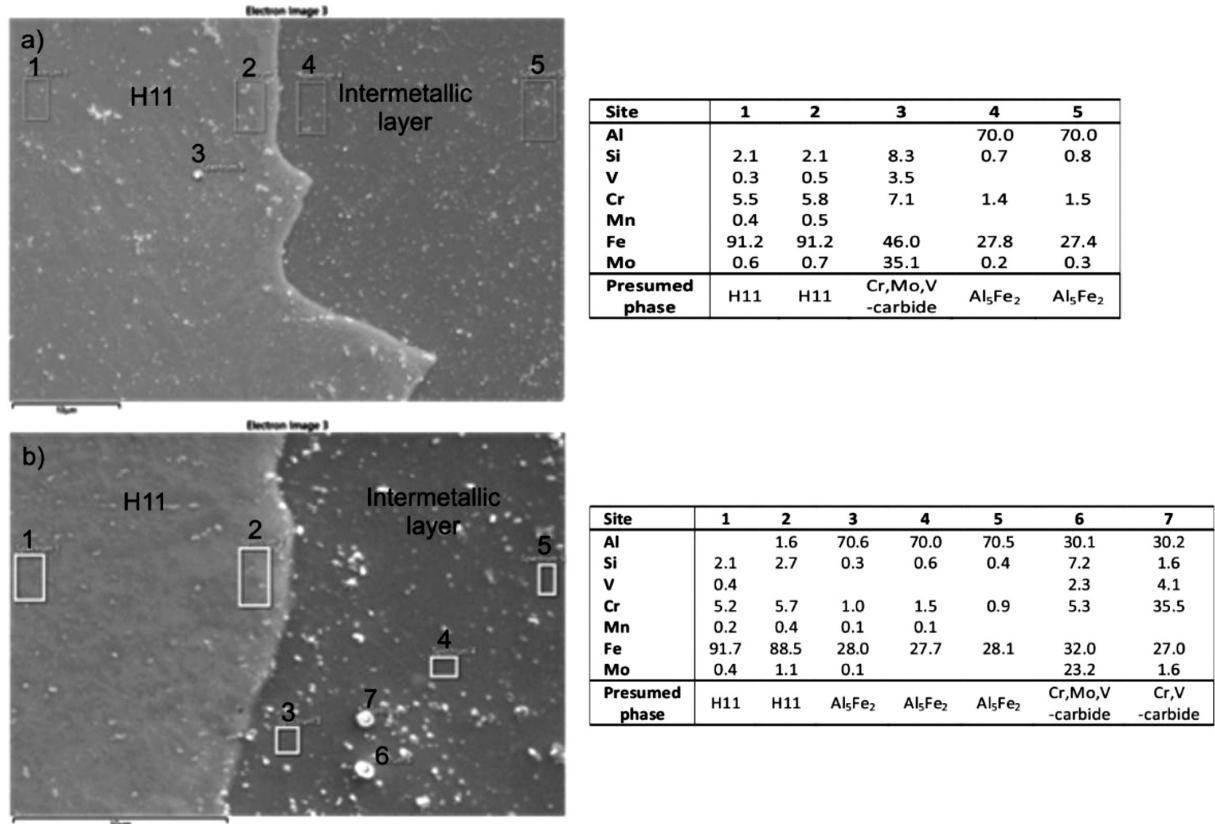


Figure 4: SEM (SEI) micrographs of the transitions between the intermetallic layer and the tool steel of samples tested at: a) 670 °C and b) 700 °C. The corresponding EDS results are given in at. %.

based on Al<sub>5</sub>Fe<sub>2</sub> (Figure 3a, site 3 and 4). This also contains a greater proportion of certain alloying elements such as cobalt, molybdenum and vanadium (Figure 4), which are present in the microstructure due to the steel. These elements form carbides, e.g., based on Mo of the M<sub>6</sub>C type, based on Cr of the M<sub>23</sub>C<sub>6</sub> type, and based on V of the MC type. These carbides can further inhibit the formation of a reaction layer and the diffusion of ele-

ments through this layer.<sup>11</sup> The silicon content in this layer increases from the aluminium alloy towards the tool steel, while the iron content increases and the aluminium content decreases (Figures 3a and 5a). This is followed by the so-called composite layer, which is formed by an intermetallic phase based on Al<sub>3</sub>Fe (site 5) and is much thicker. The analysis sites 1 and 2 in Figure 3a confirm the composition of the tool steel H11.

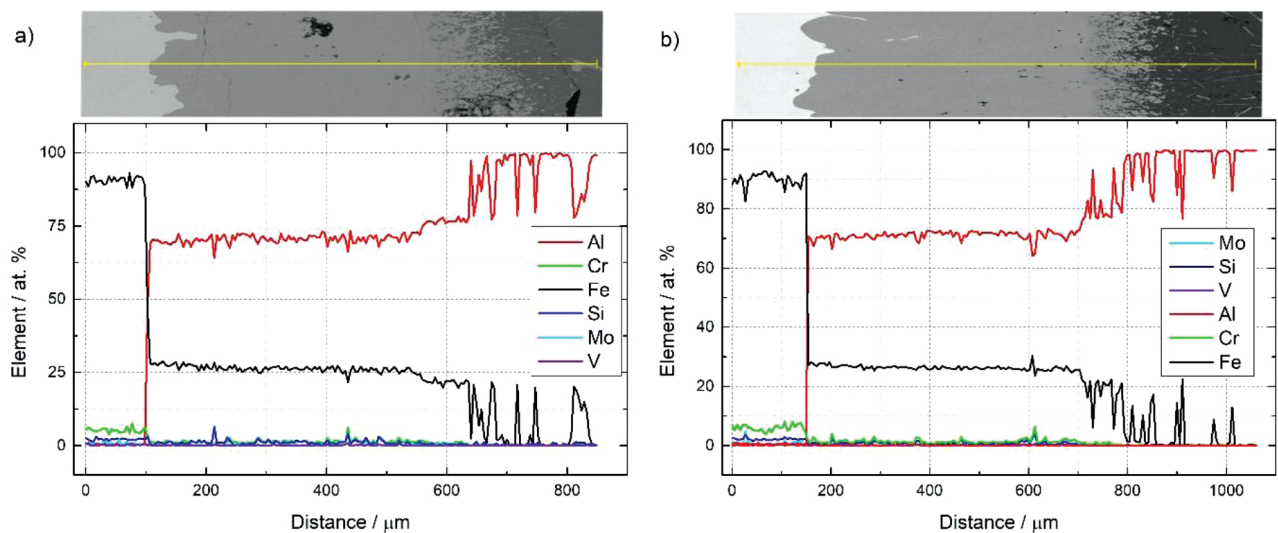


Figure 5: EDS line-scan analyses across the interface between tool-steel H11 and Al99.7 aluminium alloy tested at: a) 670 °C and b) 700 °C

Sites marked 6 and 8 represent the region of primary  $\alpha$ -Al in the presence of iron phases ( $\text{Al}_3\text{Fe}$ ), which dissolve in the molten aluminium. A similar phenomenon is observed in the sample tested at 700 °C (**Figure 3b**): tool steel (sites 1 and 2), intermetallic layer  $\text{Al}_5\text{Fe}_2$  (sites 3-5), composite layer  $\text{Al}_3\text{Fe}$  (sometimes written as  $\text{Al}_{13}\text{Fe}_4$ ) (site 6), and aluminium alloy in which iron dissolves in the form of the  $\text{Al}_{13}\text{Fe}_4$  phase (sites 8 and 9).

#### 4 CONCLUSIONS

Even very small temperature changes, in this case 30 °C, significantly affect the kinetics of the formation of interaction layers between the tool-steel H11 and molten aluminium Al99.7. All the test methods show a pronounced influence of the test temperature. From the DSC curve, a significantly faster dissolution can be seen, with the slope of the curve being larger for the sample tested at 700 °C, which was also confirmed by measurements of the thicknesses of the interaction layers. The thickness of the intermetallic layer is 520  $\mu\text{m}$  for the sample tested at 700 °C and 420  $\mu\text{m}$  for the sample tested at 670 °C. The thickness of the composite layer is about 130  $\mu\text{m}$  in both cases, which is not affected by the temperature. The types of interaction layers do not differ from each other. An intermetallic layer based on the  $\text{Al}_5\text{Fe}_2$  phase, which is thicker, always forms next to the tool steel H11, and a composite layer based on the  $\text{Al}_3\text{Fe}$  phase always forms next to the aluminium alloy.

#### 5 REFERENCES

- <sup>1</sup> M. K. Imran, S. H. Masood, M. Brandt, S. Bhattacharya, S. Gulizia, M. Jahedi, J. Mazumder, Thermal fatigue behavior of direct metal deposited H13 tool steel coating on copper alloy substrate, *Surf. Coat. Technol.*, 206 (2012), 2572–2580, doi:10.1016/j.surfcoat.2011.11.016
- <sup>2</sup> S. Zhou, Z. Qiu, D. Zeng, Deformation mechanisms and crack routes of CrAlN coatings, *Mater. Charact.*, 167 (2020), 1–6, doi:10.1016/j.matchar.2020.110491
- <sup>3</sup> H. R. Shahverdi, M. R. Ghomashchi, S. Shabestari, J. Hejazi, Microstructural analysis of interfacial reaction between molten aluminium and solid iron, *J. Mater. Process. Technol.*, 124 (2002) 3, 345–352, doi: 10.1016/S0924-0136(02)00225-X
- <sup>4</sup> G. M. Hood, The diffusion of iron in aluminium, *Philos. Mag.*, 21, (1970), 305–328, doi:10.1080/14786437008238419
- <sup>5</sup> N. A. Belov, A. A. Aksenov, D. G. Eskin, *Iron in Aluminium Alloys: Impurity and Alloying Element*, 1<sup>st</sup> ed., CRC Press, London 2002, 360, doi:10.1201/9781482265019
- <sup>6</sup> J. E. Hatch, *Aluminum: Properties and Physical Metallurgy*, ASM International, Metals Park 1984, 424, ISBN: 978-0-87170-176-3
- <sup>7</sup> A. Molinari, M. Pellizzari, G. Straffellini, M. Pirovano, Corrosion behaviour of a surface-treated AISI H11 hot work tool steel in molten aluminium alloy, *Surf. Coat. Technol.*, 126 (2000) 1, 31–38, doi:10.1016/S0257-8972(00)00530-2
- <sup>8</sup> H. R. Shahverdi, M. R. Ghomashchi, S. Shabestari, J. Hejazi, Kinetics of interfacial reaction between solid iron and molten aluminium, *J. Mater. Sci.*, 37 (2002), 1061–1066, doi:10.1023/A:1014324603763
- <sup>9</sup> N. Tang, Y. Li, Y. Koizumi, S. Kurosu, A. Chiba, Experimental and theoretical research on interfacial reaction of solid Co with liquid Al, *Corros. Sci.*, 73 (2013), 54–61, doi:10.1016/j.corsci.2013.03.024
- <sup>10</sup> M. Vončina, T. Balaško, J. Medved, A. Nagode, Interface reaction between molten Al99.7 aluminium alloy and various tool steels, *Materials*, 14 (2021) 24, 7708, doi:10.3390/ma14247708
- <sup>11</sup> V. G. Gorbach, V. G. Alekhin, G. L. Kurganova, Determining thermal fatigue of steels for die casting of aluminum alloys, *Met Sci Heat Treat*, 19 (1977), 982–985, doi:10.1007/BF00670172
- <sup>12</sup> M. Vončina, S. Kores, A. Nagode, T. Balaško, Study of interaction between molten aluminium and hot-work tool steel using DSC method, *J. Therm. Anal. Calorim.*, 146 (2021), 1091–1099, doi:10.1007/s10973-020-10069-3