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REACTIVE-SINTERING PRODUCTION OF INTERMETALLICS

IZDELAVA INTERMETALNIH ZLITIN Z REAKTIVNIM SINTRANJEM

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Intermetallic phases offer a large variety of interesting properties, such as high-temperature oxidation resistance, creep resistance, special magnetic properties, shape memory or the ability to store hydrogen reversibly. However, the practical utilization of this group of materials is very limited due to problematic production. Casting is commonly applied to produce many of these materials, even though there are strong limitations of this technology, such as high melting points and poor casting properties. Powder metallurgy involving the reactive sintering of compressed mixtures of elemental powders is one of the promising alternative production routes. In this work, the preparation of several technically important intermetallics was tested. Aluminide- and silicide-based high-temperature materials and NiTi shape-memory alloys were successfully produced with this technique.

Keywords: intermetallics, powder metallurgy, reactive sintering

Intermetalne faze imajo vrsto zanimivih lastnosti, kot so visoka temperaturna odpornost za oksidacijo, odpornost proti lezenju, posebne magnetne lastnosti, oblikovni spomin ter sposobnost reverzibilnega shranjevanja vodika. Vendar pa je praktična uporaba te vrste materialov močno omejena zaradi njihove problematične izdelave. Ulivanje se uporablja pri številnih teh zlitinah za njihovo proizvodnjo, čeprav obstajajo omejitve pri tej tehnologiji, kot so visoke temperature tališča in slaba livnost. Ena od obetajočih mogočih poti za njihovo proizvodnjo je prašna metalurgija, ki vključuje reakcijsko sintranje stisnjenih mešanic elementnih prahov. V tem delu je bila preizkušena izdelava več tehnično pomembnih intermetalnih zlitin. S to tehniko so bili uspešno izdelani visokotemperaturni materiali na osnovi aluminidov in silicidov ter zlitina NiTi s spominom.

Ključne besede: intermetalne zlitine, prašna metalurgija, reaktivno sintranje

1 INTRODUCTION

Intermetallics are formed in many alloy systems when the concentration exceeds the solubility limit. These materials exhibit properties totally different from the common metals forming them. They can usually be recognized by a high melting temperature, excellent oxidation resistance at high temperatures and very good mechanical properties at high temperatures. The intermetallics for high-temperature service are also characterized by a low density since they are usually based on a system of a transition metal and aluminium (Ti-Al, Fe-Al, Ni-Al). Some intermetallic compounds also exhibit many interesting properties, such as shape memory (Ni-Ti) or hydrogen-storage ability (La-Ni, Mg-Ni). However, the application potential of these materials is limited by low room-temperature ductility and also by problematic production. Common production and processing routes of intermetallics are melting and casting[1]. Considering high melting points, enormous reactivity of the melts with oxygen and crucible materials (mainly in the case of the Ti-based intermetallics)[2] and poor casting properties, this process is bound to be very problematic. Because of the limited plasticity of several intermetallics even at high temperatures, forming processes are not recommended for many intermetallics except for NiTi and special hot-working processes developed for FeAl.[3] Therefore, powder metallurgy starts to play an important role in the production of intermetallic compounds. Conventional powder-metallurgy techniques using the powders of intermetallic phases are applied, but they are also very complicated due to poor compressibility and sinterability of the intermetallic powders. Due to these facts, reactive-sintering powder metallurgy seems to be a promising alternative. In this process, the powders of metals or alloys are blended and compressed. Intermetallics are formed during the subsequent sintering process by thermally activated chemical reactions[4]. The aim of our experiments was to test the applicability of this method for the production of technically important intermetallics.

2 EXPERIMENTAL WORK

Metallic powders of 99.9 % purity were blended in desired proportions and compressed at room temperature by a pressure of 320 MPa using a Heckert FPZ 100/1 universal loading machine. Pressureless reactive sintering of the obtained green bodies (Fe-Al, Ti-Al, Ni-Al, Fe-Al-Si, Ti-Al-Si, Ni-Ti) was carried out at 1100 °C. The microstructure and porosity of the products were investigated. Cyclic oxidation tests were carried out at 800 °C in air. The oxidation rate was determined from the gain in mass caused by the oxide formation on the surface of the thermally exposed samples. The abrasive wear resistance was evaluated using a modification of the pin-on-disc method, where the pin was the tested material and the disc was P1200 grinding paper. The applied load was 5.8 N and the sliding distance was defined as 2.5 km. The wear rate was calculated from the measured mass losses using the equation (1):[5]

$$w = \frac{\Delta m \cdot 1000}{F \cdot \rho \cdot l} \tag{1}$$

where w, Δm, F, ρ and l are the wear rate [$mm^3\ m^{-1}\ N^{-1}$], the mass loss [g], the normal force [N], the density [$g\ cm^{-3}$] and the sliding distance on the grinding paper [m], respectively. The density of the samples was determined with the Archimedes method.

3 RESULTS

When the transition-metal aluminides are produced with reactive sintering, the aluminium melts prior to the reactions. The molten aluminium reacts immediately with the transition metal producing aluminides. Due to the presence of the transient liquid phase, a low porosity of the product can be expected. On the other hand, most of the aluminides produced with reactive sintering (e.g., FeAl, TiAl) form highly porous structures with a porosity exceeding the volume fraction $\varphi = 30\ \%$, see **Figures 1a, b** and **Table 1**. In the case of the Ni-Al system, a low-porosity product can be obtained (**Figure 1c**).

Table 1: Porosity, hardness (HV 10) and abrasive wear rate (w) of the high-temperature materials produced by reactive sintering

Tabela 1: Poroznost, trdota (HV 10) in hitrost abrazijske obrabe (w) visokotemperaturnega materiala, izdelanega z reakcijskim sintranjem

	Porosity, φ/%	HV 10	w/ ($mm^3\ m^{-1}\ N^{-1}$)
NiAl30	2	306	0.0045
FeAl28	35	350	0.004
TiAl45	31	450	0.0025
FeAl20Si20	8	860	0.0004
TiAl15Si15	7	750	0.0003

When a suitable alloying element is introduced to a transition metal – an aluminium system - the reaction mechanism can be affected, leading to a porosity reduction. In the case of aluminides, silicon can modify the reaction mechanism with the formation of silicides and/or ternary phases with aluminium and silicon (**Figure 2**). With an addition of silicon, porosity reduces to less than $\varphi = 8\ \%$ in both Fe-Al- and Ti-Al-based systems. The

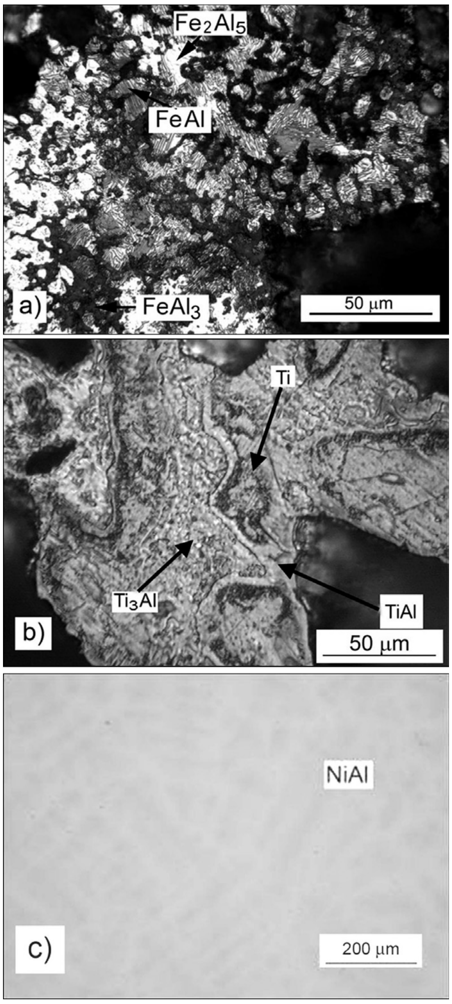

Figure 1: Microstructures of: a) FeAl40, b) TiAl36, c) NiAl30, prepared by reactive sintering at 1100 °C for 15 min

Slika 1: Mikrostruktura zlitin: a) FeAl40, b) TiAl36, c) NiAl30, pripravljenih z reakcijskim sintranjem 15 min na 1100 °C

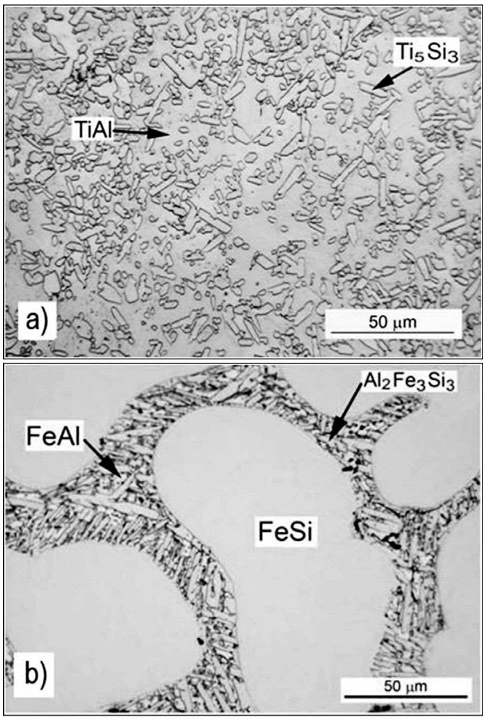

Figure 2: Microstructures of: a) TiAl15Si15 and b) FeAl20Si20, prepared by reactive sintering at 1100 °C for 15 min

Slika 2: Mikrostruktura zlitin: a) TiAl15Si15 in b) FeAl20Si20, pripravljenih s 15-minutnim reakcijskim sintranjem na 1100 °C

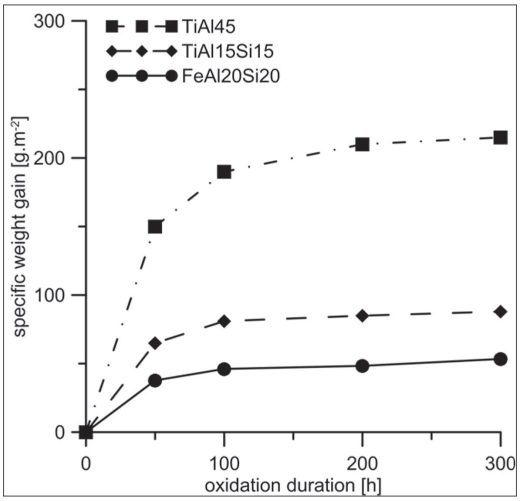

Figure 3: Oxidation resistance of Fe-Al- and Ti-Al-based alloys at 800 °C in air

Slika 3: Odpornost proti oksidaciji zlitin na osnovi Fe-Al in Ti-Al pri 800 °C na zraku

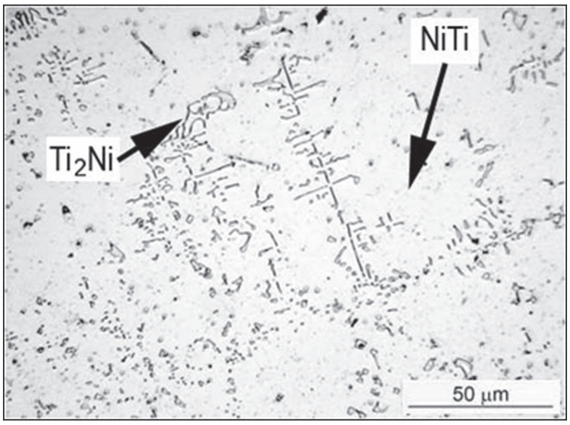

Figure 4: Microstructure of the NiTi alloy, prepared by reactive sintering at 1100 °C for 15 min

Slika 4: Mikrostruktura zlitine NiTi, pripravljene z reakcijskim sintranjem 15 min na 1100 °C

optimum addition of silicon is between mass fractions 10 % and 20 %. TiAl15Si15 is formed with fine round-shaped Ti_5Si_3 particles dispersed in the TiAl matrix (**Figure 2a**). The structure of the FeAl20Si20 alloy is more complex. It consists of the FeSi and FeAl binary phases as well as of the $Al_2Fe_3Si_3$ ternary one (**Figure 2b**).

The properties of the prepared materials are shown in **Table 1** and **Figure 3**. In addition to the porosity discussed above, a silicon addition also improves the hardness, the wear resistance and the high-temperature oxidation resistance of these materials.

The other group of the intermetallics with a large application range includes the shape-memory alloys. The reactive-sintering powder-metallurgy technique was tested also for the production of these materials. The NiTi phase was produced with reactive sintering under the same conditions as the previous alloys. Porosity below $\varphi = 4$ % was achieved. The product contained the desired NiTi shape-memory phase, as well as a low fraction of the Ti_2Ni phase (**Figure 4**).

4 DISCUSSION

It was shown above that the binary aluminides produced with the pressureless reactive-sintering process are extremely porous. When silicon is added the porosity is reduced in both the Fe-Al-Si and Ti-Al-Si alloys. In the literature this is generally attributed to an unbalanced diffusivity of the transition metals and aluminium[2]. In addition, it has been believed that in a Fe-Al system, the Fe_2Al_5 phase forms in the solid state, before the aluminium starts to melt[6]. However, this explanation was already disclaimed by the current in-situ XRD measurements. These new results indicate that during a faster heating Fe_2Al_5 (and probably also FeAl) forms immediately after the melting of aluminium. In our previous paper[7] this can be observed as one exothermic peak on the heating curve of the differential thermal analysis, being superposed from these exothermic processes and the endothermic melting of aluminum. A silicon addition probably prolongs the interval prior to the formation of the first phase, because silicon forms a eutectic with the aluminum melting at about 580 °C. In the presence of silicon, the reactions are more exothermic and therefore the reaction mixture can be partially remelted during the reactive sintering. In the NiAl system, the reactions are more exothermal than in Fe-Al or Ti-Al and therefore the heat is probably sufficient for a partial melting of the green body during the reactive-sintering process.

A positive effect of a silicon addition on the oxidation resistance, hardness and wear resistance of the Fe-Al and Ti-Al alloys is the presence of the silicon-rich phases such as Ti_5Si_3 or FeSi silicides and $Al_2Fe_3Si_3$ or other ternary phases. All of these phases are very hard, thus improving the reinforcement. They increase the overall hardness and wear resistance of the produced materials that are almost comparable with the superior heat-treated cold-work tool steels. However, in these materials the above phases can be achieved without any heat treatment. Therefore, it seems that the silicon-alloyed intermetallics can probably be seen as the candidate tool materials. To prove their applicability, the fracture toughness and the fatigue resistance of these materials have to be checked and the porosity minimized by optimizing the processing technology.

In the case of the NiTi shape-memory alloy, the phase composition obtained corresponds to that of the cast material. The undesirable Ti_2Ni phase can be eliminated with the consequent heat-treatment and the final shape is obtained by hot forming as usual when NiTi is produced with the conventional melting technique. The biggest advantage of the reactive-sintering technology is the elimination of the contamination of the product from the melting crucible or from the other parts that come in contact with the melt.

5 CONCLUSIONS

Reactive-sintering powder metallurgy was proved to be a useful method for producing the multiphase Fe-Al-Si and Ti-Al-Si alloys as well as the NiAl binary phase. These intermetallics are promising light materials for high-temperature applications. Due to an enormous hardness and wear resistance, the above mentioned ternary alloys can also find other application fields, e.g., tool materials.

The synthesis of a NiTi shape-memory alloy was also successful. The advantage of this technology lies in a lower contamination of the product than found in the common melting processes.

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