Intermetallics as innovative CRM-free materials

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Abstract. Many of currently used technical materials cannot be imagined without the use of critical raw materials. They require chromium (e.g. in stainless and tool steels), tungsten and cobalt (tool materials, heat resistant alloys), niobium (steels and modern biomaterials). Therefore there is a need to find substitutes to help the European economy. A promising solution can be the application of intermetallics. These materials offer wide variety of interesting properties, such as high hardness and wear resistance or high chemical resistance. In this paper, the overview of possible substitute materials among intermetallics is presented. Intermetallics based on aluminides and silicides are shown as corrosion resistant materials, composites composed of ceramics in intermetallic matrix as possible tool materials. The manufacturing processes are being developed to minimize the disadvantages of these materials, mainly the room-temperature brittleness.

1. Introduction

Metallic materials are used in structural applications for their typical properties, such as good strength and toughness at common temperatures, ductility, electric and thermal conductivity etc. In addition to this common application range, the use at the limits of these materials is also often required, e.g. at high temperatures, in strongly aggressive corrosion environment or under extreme abrasive or adhesive wear. High temperatures are very problematic for common metallic materials due to oxidation and gradual degradation by creep. For high-temperature application, iron-based alloys (i.e. heat resistant steels), nickel and cobalt alloys are commonly applied. However, these materials are characterized by relatively high density (7.8 - 9 g.cm⁻³), which is strongly disadvantageous e.g. for aerospace industry. Another important problem for EU economy is the fact that these materials contain elements (e.g Co, W), which are listed by European Commission as critical raw materials (CRM) [1]. Similar problem is in the case of tool materials, which contain Co and W as the main constituents (cemented carbides) and also elements with high economic risk just below the boundary defining CRMs (Cr, Mo). In addition, high resistance against mechanical wear is achieved by heat treatment in the case of tool steels and therefore the operating temperature is limited by the tempering temperature. Materials based on intermetallics could be promising substitutes of these materials. Intermediate phases are formed in many systems of two or more metals or metals with non-metals when the solubility in metal-based solid solution is exceeded. Intermediate phases are chemical
compounds whose structure differs from all elements forming them. If they contain metals only, they are called intermetallic phases or intermetallic compounds, abbreviated as intermetallics. Compounds of metal with semimetal (silicides) and ordered solid solutions of aluminium in transition metals (aluminides, e.g. FeAl, Fe₃Al) are also usually denoted as intermetallics. This paper aims to present the possible outlooks in application of intermetallic compounds as CRM substitutes.

2. Heat and corrosion resistant materials
The application as high temperature materials is probably dominant in the case of intermetallics. High melting points (e.g. 2130 °C for Ti₅Si₃ [2]), good creep properties and high-temperature oxidation resistance predestine them to this application range. Typical intermetallics for high temperatures are silicides (e.g. MoSi₂) for heating elements of electric resistance furnaces and nickel aluminides used mainly in the form of protective coatings for turbine blades for power plants. In addition to these materials, Ti-Al phases (mainly Ti₃Al a TiAl) and the ordered Fe₃Al a FeAl phases play an important role.

During the development of intermetallics based on Fe-Al and Ti-Al systems, the positive effect of Cr, W and Nb has been proved and therefore current commercial variants of these materials used e.g. in airplane jet engines are commercially produced [3]. However, these elements are listed as CRMs [1]. It has been also proved that the addition of silicon decreases the oxidation rate of Ti-Al alloys at the temperatures up to 1000 °C (Figure 1). Similarly, highly positive effect of silicon was found in the case of Fe-Al alloys. In both of these groups of materials, the silicon addition leads to the improvement of the protective properties of the oxide layer and also to the formation of silicides and other oxidation-resistant silicon-rich phases under the oxide layer (Figure 2) [4]. This sub-layer acts as a secondary barrier against oxygen penetration to the material, thus lowering the oxidation rate and protecting the core of the material. Due to these findings, further research was focused on Ti-Al-Si and Fe-Al-Si alloys. Silicon use can be managed even though it is also listed as CRM. As a source of this element, the secondary silicon from recycled electronics can be applied, because lower purity is required in these alloys. In addition, the silicon is listed as CRM probably mainly due to the lack of manufacturing capacities (silicon production plants) in Europe, even though there are relatively large reserves of the raw material (silica).

![Figure 1: Oxidation resistance of Fe-Al-Si and Ti-Al-Si alloys at 800°C in air](image-url)
Systematic testing of the influence of the other alloying elements on the properties of these materials led to the development of Fe-Ni-Al-Si alloy, which exhibits much lower density than common high-temperature materials (approx. 6 g.cm$^{-3}$) together with excellent oxidation resistance, thermal stability and relatively low price of the constituents [5].

It has been proved that the iron and titanium aluminides are also corrosion resistant in electrolytes [6]. Iron aluminide (FeAl) passivates by the Al$_2$O$_3$ layer in the solutions with pH above 3. Similar situation is for titanium aluminide, where this limit is at the pH of 2.5 - 3. When the material is alloyed by silicon, it is able to passivate by a layer of silicon oxide even below these values, but the passive layer is weaker.

3. Tool materials

The above mentioned aluminium and silicon alloyed materials exhibit also high wear resistance [7]. These properties predispose this alloy not only to the highly demanding high-temperature applications, but probably also for e.g. the high-speed machining tools, where high wear resistance and thermal stability are required. Other materials, which are the candidates for severe wear conditions as in tools are the composite materials with intermetallic matrix and ceramic reinforcement. One example of this type of materials is the composite with NiAl matrix reinforced by particles or short fibres of Al$_2$O$_3$ (Figure 3). This composite was successfully prepared by three powder metallurgy methods – reactive sintering of the mixture of nickel and titanium powders with alumina particles or short fibres [8], aluminothermic reaction between nickel oxide and aluminium [8], mechanical alloying of the mixture of nickel and aluminium with the addition of alumina particles and subsequent compaction by spark plasma sintering.

**Figure 2**: Microstructure of the near-surface area of the Ti-Al-Si alloy after oxidation [4]
4. Processing of intermetallics

In processing of intermetallics, the casting technology is dominant, even more than in the case of conventional metallic materials. The reason is limited plasticity even at higher temperatures, which makes the forming processes feasible only in individual cases [9]. Ti-Al-Si and Fe-Al-Si alloys manufactured by melting and casting contain coarse, randomly oriented sharp-edged particles rich in silicon (Figure 4a). In the structure of Ti-Al-Si alloy this particle can be identified as Ti$_5$Si$_3$ silicide, while in Fe-Al-Si alloys a large series of various silicon-rich phases can be seen depending on the silicon content. There are FeSi and Fe$_3$Si silicides or Fe-Al-Si ternary phases (e.g. Al$_2$FeSi, Al$_2$Fe$_3$Si$_3$ or Al$_2$FeSi$_3$). These intermetallics are highly oxidation resistant, but also very brittle. This fact leads to undesirable mechanical properties. Therefore, the processes for modification of the morphology of these phases were searched in order to eliminate this negative influence. The first approach was the experiment with the orientation of the Ti$_5$Si$_3$ particles, aiming to produce in-situ composite by elongated Ti$_5$Si$_3$ particles (fibres) in tougher matrix composed of Ti$_3$Al or TiAl phases. Directional solidification experiments were carried out in floating zone optical furnace in cooperation with the Institute of Physics AS CR. However, there were cracks in silicide fibres observed in the directionally solidified structure (Figure 4b). The reason for this phenomenon is different thermal expansion coefficient of Ti$_5$Si$_3$ silicide in dependence on crystal direction. Due to this fact, the stress is formed arising in the initiation of cracks. It strongly limits the applicability of Ti-Al-Si alloys produced by directional solidification [10]. Following research was focused on refinement of silicon-rich phases by powder metallurgy. Powder metallurgy processes used in production of intermetallics can be divided to two main groups. First one comprises the processes using the alloyed powders, i.e. already produced intermetallics. Alloyed powders can be prepared by milling of compact materials prepared by casting, melt atomization or by direct milling of elemental powders - by mechanical alloying [11]. The latter technology is able to prepare nano-grained powders (Figure 4c). However, this process is highly energy consuming. The next disadvantage of this technology is problematic densification of the powders of intermetallics. These powders are characterized by problematic compressibility and sinterability and therefore the consolidation requires application of special techniques, such as Hot Isostatic Pressing (HIP) or Spark Plasma Sintering (SPS). SPS technology is a modern process which uses compression and simultaneous passage of high electric current (e.g. 4000 V). It leads to rapid heating of the material
and formation of discharge between the powder particles, resulting in fact in local welding of the powders to form compact material [12]. In order to lower the porosity of the product and to improve the mechanical properties correspondingly, the High Pressure Spark Plasma Sintering (HP SPS) has been developed and also already applied to intermetallics [13].

Second group of the powder metallurgy methods in production of intermetallics comprises the reaction synthesis processes using the chemical reactions between the powders of pure metals or alloys. In these processes called reaction sintering, the intermetallics are formed by thermally activated reactions between metallic powders. The initiation proceeds usually at the temperatures significantly lower than the melting point of prepared compound. Therefore the chemical reactions leading to the formation of intermetallics are usually strongly exothermic and therefore it is not needed to supply the heat after initiation and thus the reactions propagate by its own evolved energy. Due to this fact, this technology is often called SHS - Self-propagating High-temperature Synthesis [14]. Especially suitable seem to be the systems, where one reactant (e.g. aluminium) is molten before initiation. It fills the pores by capillary forces and decreases the porosity of the product. Nevertheless in the case of intermetallics in Fe-Al and Ti-Al systems reach the porosity above 25 vol. % [14,15]. The phenomenon is associated predominantly with significantly different diffusion rate of aluminium and iron or titanium, where the unidirectional diffusion is compensated by the diffusion of vacancies, and also with the temporary formation of phases with totally different structure (e.g. Fe$_2$Al$_5$). It leads to volume changes causing the porosity [16].

The research carried out in our department showed that the ternary alloys with silicon do not suffer from this problem. The reasons are in different mechanism of the reactions and also in high thermal effects in presence of silicon. It can cause local melting of the reaction mixture [17].

Figure 4: Microstructure of the Ti-Al-Si alloy prepared by: a) casting, b) rapid solidification, c) mechanical alloying and spark plasma sintering, d) reactive sintering [10,17]
After optimization of the conditions, the porosity of less than 7 and 4 vol. % was achieved for Ti-Al-Si and Fe-Al-Si alloys, respectively [10,11] (Figure 4d). Further lowering of the porosity can be achieved by use of pressure-assisted reactive sintering. In addition, the products of this technology are very fine in comparison with the common cast materials. The particles of silicides and ternary phases reach rounded shapes on the contrary to cast alloys (Figure 4a). It positively influences the mechanical and tribological properties [17].

5. Conclusion
Intermetallics are already used as substitutes of CRM-containing materials in selected applications (e.g. jet engines and furnace elements) and their importance will probably grow. However, the extensive development and positive reaction of the industry is still needed. For this purpose, the CA15102 action is a very important tool. The modern powder metallurgy technologies were presented as efficient tools for processing of technically important intermetallics.

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