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Review Article

An overview of intermetallics research and application: Status of thermal spray coatings

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ABSTRACT

The aim of this review is to update and to offer an overview of the investigations that have more recently been made on intermetallics, to highlight their importance for several applications in many areas and to examine topics for future research. The main subject is the application of intermetallics as thermal spray coatings. This will allow balancing the discussion of whether they are promising as a surface medium for materials that work at high temperatures. The general intermetallics classification includes iron, nickel, and titanium aluminides, as well as transition metal silicides. As nickel aluminides have been important in issues related to bonding coats, their research trajectory has been revised. Moreover, as the Fe-Al system has also been studied in terms of thermal spray processing, its good characteristics have also been assessed. The third intermetallic this article focuses on is NiTi, which appears not to be included in general classifications of intermetallic compounds, but it deserves to be mentioned mainly due to its shape memory effect and biocompatibility properties.

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1. Introduction

Despite the fact that it is not an issue that is frequently discussed, the first study about intermetallic compounds dates to the beginning of the last century, thanks to investigations carried out by Kumakov et al. [1] in 1916 on the system Au-Cu. During the 1950's, the scientific research underwent an important increase, but as rapid as it had arisen, it decreased during the subsequent decade due to the major drawback of the lack of ductility of such compounds. Afterwards, it was not until the discoveries of Aoki and Izumi [2] in the 1980's that knowledge about intermetallic compounds became important again. Thus, although the impact of intermetallic compounds on the metallurgical community has been unremarkable for a very long time, it is now changing basically due to the challenge of finding strengthening, tenacious, and ductile materials at high temperatures that are able to substitute superalloys [3], which have been able to satisfy the demands for high temperature applications until now. However, there is a current trend to supply even higher efficiency by reaching

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higher service temperatures, and therefore, since superalloys have melting points lower than 1,400 °C, new materials will be demanded, such as those called by Tanaka [4] 'ultra-high temperature materials' (presented in Table 1), which he explores in his research paper about their development activities.

1.1. General intermetallic compounds concepts

Unlike conventional metal alloys, which could be described as a base material to which certain percentages of other elements have been added, intermetallic compounds have a particular chemical formula with a fixed or narrow range of chemical composition. In addition, instead of their atoms being linked with relatively weak metallic bonds, the bonding may be partly ionic or covalent, which gives them an ordered crystal lattice. Some intermetallics can even keep this order until their melting point, which is the main reason why they possess strong stability at high temperatures [3,5].

Several authors have attempted to define the best way to describe intermetallic phase structures such as Schubert [6] in 1964 and Frevel [7], in 1985; however, once Strukturbericht notation became widespread, the most commonly used designation became the system of Pearson symbols (Table 2); this system consists of a sequence of two letters and a number. The first (small) letter corresponds to the crystal system of the structure type involved; the second (capital) letter represents the lattice type. The symbol is completed by the number of atoms in the unit cell. According to this system, one can see some examples in Fig. 1 [8], where the Strukturbericht designation is accompanied by the Pearson symbol in parentheses.

An interesting concept worth mentioning is the term of ordering energy, which is used to identify the work that must be done to a perfectly ordered alloy so that it loses its order. It is clearly smaller than the formation energy of the compound from the elements. In intermetallics, the ordering energy is especially important because the intermetallics' long-range order is highly related to their creep properties as reviewed by Cahn [9]. Apart from introducing the concept of ordering energy and how it can be measured, the author revises possible methods such as mechanical milling or ultrarapid solidification to disorder ordered phases. One of its conclusions is that diffusivity is the responsible of creep resistance behavior, and the higher the ordering energy, the lower the probability of intermetallic disorders. A closely related study also carried out by Cahn [10] attempts to discover a relationship between lattice parameter changes and ordering energy or radius mismatch of the constituent atoms. From the obtained results, Cahn concludes that the lattice parameter changes are correlated much more closely with the ordering energy than with the mismatch of atomic sizes.
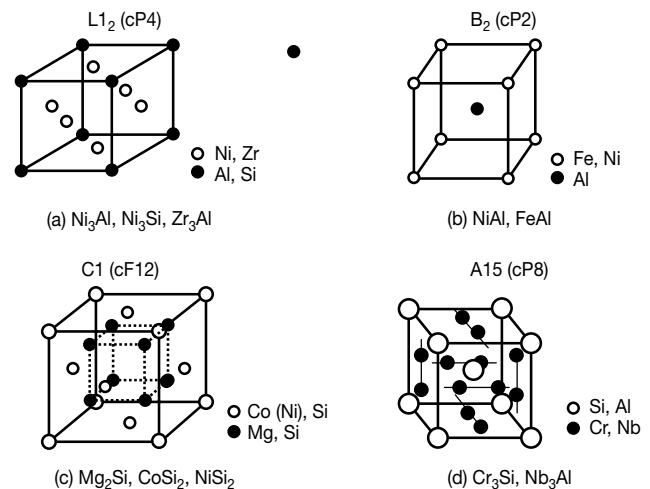

Fig. 1 – Generic cubic lattices.

Table 1 – A classification of the ultra-high temperature materials [3].	
Metallics	Intermetallic compounds (IMCs): TiAl, NiAl, $MoSi_2$, Nb_3Al, etc.
	Refractory metals and alloys: W, Ta, Mo, Nb, etc.
Ceramics	Oxides: Al_2O_3, SIALON, Al_2O_3/YAG directionally solidified eutectic (MGCMelt growth composite), etc.
	Non-oxides: SiC, Si_3N_4, etc.
Composites	Metal matrix composites (MMC): SiC/Ti, SiC/TiAl, W/Superalloy, etc.
	Ceramic matrix composites (CMC): SiC/SiC, SiC/LAS, C/SiC, etc.
	Carbon/carbon composites (C/C): C/C
	Functionally graded materials (FGM): TiB/Ni, Al_2O_3+ZrO_2/Ni, etc.

Table 2 – Pearson symbols.	
System symbol	Lattice symbol
a (triclinic, anorthic)	P (primitive)
m (monoclinic)	I (body centered)
o (orthorhombic)	F (all-face centered)
t (tetragonal)	C (side face centered)
h (hexagonal and trigonal and rhombohedral)	R (rhombohedral)
c (cubic)	

Table 3 – General characteristics of selected intermetallic compounds [11].					
Intermetallic	Crystal structure	Critical ordering temperature (°C)	Melting point (°C)	Density (g/cm^3)	Young's modulus (GPa)
Ni$_3$Al	L1$_2$ (fcc)	1,390	1,390	7.50	179
NiAl	B2 (bcc)	1,640	1,640	5.86	294
Fe$_3$Al	D0$_3$ (bcc)	540	1,540	6.72	141
	B2 (bcc)	760	1,540	–	–
FeAl	B2 (bcc)	1,250	1,250	5.56	261
Ti$_3$Al	D0$_{19}$ (hcp)	1,100	1,600	4.2	145
TiAl	L1$_0$ (tetragonal)	1,460	1,460	3.91	176
TiAl$_3$	D0$_{22}$ (tetragonal)	1,350	1,350	3.4	–
NiTi	Martensite	Transformation temp.	1,300	6.45	28-41
	Austenite	–200 °C to 110 °C	1,300	6.45	83

The main properties of intermetallics can be summarized as follows [3,5,11]: high melting points; high thermal conductivity; low densities; great strength, particularly at high temperatures; good oxidation resistance at high temperatures (because of the formation of oxide films); low ductility; brittle fracture at room temperature; and processing problems.

The main groups within which they can be classified are: nickel aluminides, iron aluminides, titanium aluminides and others such as silicides, nickel titanium, and refractory metal aluminides. Aluminides are especially interesting because, for most of them, their ordering temperature is close to the melting temperature. Within this group, many exist over a range of compositions, but the degree of order decreases as the deviation from stoichiometry increases [11]; iron, nickel and titanium-based intermetallics provide a good mechanical strength/mass ratio and oxidation resistance to high temperatures, despite the lack of knowledge about creep and fatigue resistance. As it appears, they cannot compete with superalloys due to their relative low creep resistance, apart from their poor ductility. However, some researchers intend to solve this problem by precipitation and solid solution hardening [12] or even by dispersing particles, which affect creep properties by performing as dislocation obstacles [13]. General characteristics of the main aluminides and other intermetallics are presented in Table 3. As can be seen, some of them are weakly ordered superlattices due to their long-range order loss simply by heating to a transition temperature well below the melting temperature, whereas others can be called permanently ordered phases as they conserve the order until their melting points.

In general, aluminides of transition metals possess sufficient concentration of aluminum to form an adherent alumina layer when exposed to air or oxygen atmospheres. This interesting property leads to the fact that they exhibit an outstanding oxidation and corrosion resistance in aggressive chemical environments and even at temperatures as high as 1,000 °C or more [11].

1.2. Research and development on intermetallics

Apart from their corrosion and oxidation resistance, it is worth mentioning that researchers have strived to create intermetallics with better ductility. Therefore, different attempts are based on the addition of alloying elements, especially boron, and others such as Zr, Cr, and Si, as well as adding alloying elements. Reducing grain size can also enhance ductility, improving fracture toughness at room temperature. In addition, the current research is based on finding rare earth intermetallic compounds that are ductile at room temperature and developing exotic intermetallics with potentially high working temperatures [14].

The low feasibility of making anything useful from intermetallic compounds raised the idea to investigate their use as a surfacing medium. Some successful results have been obtained using thermal spray technologies. Consequently, this issue will be mainly focused on the following sessions, especially for Fe and Ni aluminides and NiTi. Although there is currently a great deal of knowledge about TiAl-based alloys, those materials are not discussed in the present work. However, some literature is proposed for specific studies.

2. Specific characteristics, research and application

2.1. FeAl intermetallics

FeAl intermetallics have been intensively studied to prove whether it is possible to substitute high temperature or stainless steels and superalloys in some applications. They possess enough high concentrations of aluminum to form a continuous and adherent alumina layer on the surface when exposed to air or oxygen atmospheres. The heat of formation and aluminum percentages of FeAl intermetallics can be seen on Table 4. Possible industrial applications are: heat-treating

Table 4 – Weight percentages of aluminum and heats of formation of FeAl intermetallics [5].		
Intermetallic	Weight percent (wt%) of Al	Heat of formation, ΔH_{298} (kcal/mol)
Fe$_3$Al	13.87	–16.0
FeAl	32.57	–12.0
FeAl$_2$	49.1	–18.9
Fe$_2$Al$_5$	54.70	–34.3

trays, immersion heaters, porous filters, automotive piston valves and automotive exhaust systems, centrifugally cast tubes, radiant tubes for heat exchangers and catalytic conversion vessels.The most frequently studied compositions are 20 at.% and 40 at.% Al. These are related to the Fe3Al and FeAl chemical formulae. Actually, as can be extracted from the phase diagram, FeAl (single phase) exists over the composition 36 at.% to 50 at.% Al. With regards to Fe3Al, the transition temperature between the two observed ordered structures (D03 and B2) decreases and the B2 ordering temperature increases as the aluminum content is enhanced.

FeAl presents a B2 (cP2) crystal lattice, which comes from the body-centered cubic structure. The unit cell contains 8 aluminum atoms, 1 in each corner, which are shared with the other 8 unit cells surrounding the 1 aluminum atom, which is typical for the bcc structure. As the cP2 structure can be seen as 2 interpenetrating primitive cubic cells, the iron or nickel atoms are supposed to occupy the corner of the second sublattice.

Fe$_3$Al has the ordered cubic D0$_3$ (cF16) crystal structure. This unit cell contains 8 bcc type subcells and it may be thought of as being composed of 4 interpenetrating fcc lattices. In each subcell the iron atoms occupy corners, and thus, each of them is shared with 8 neighboring subcells, resulting 1/8 of the iron atom per subcell. Furthermore, 4 iron atoms occupy the centers of 4 subcells, so there are 12 iron atoms in the D0$_3$ unit cell. Including the 4 aluminum atoms, which also occupy the centers of 4 subcells, the total number of atoms per unit cell comes to 16. Fe$_3$Al transforms to B2 (cP2) structure at temperatures above 540 °C.

In general the characteristics of iron-based intermetallic alloys are: better resistance to sulphidation than any other iron or nickel-based alloys; high electrical resistivity, which increases with temperature; good corrosion resistance; low material cost; and poor creep and high temperature strength above 500 °C. Table 5 shows relevant information about the Fe-Al system and its characteristic reactions. Regarding the mechanical properties, as well as for NiAl, the yield strength and fracture mode depend on the aluminum content; above or

below 40 at.% Al content, this intermetallic shows intergranular or transgranular fracture, respectively, which is extensively explained by Liu and Stiegler [11]. Regardless, the main reasons behind the brittle fracture in Fe$_3$Al are the environmental effects, while in FeAl, it must be also considered grain boundary weakness and vacancy hardening [16]. However, contrary to NiAl behavior, FeAl strength and hardness increase near to stoichometric composition. While coarse-grained FeAl-based materials (below 40 at.% Al) exhibit a small increase of yield strength with temperatures reaching a maximum of 550 °C to 650 °C, an atomic aluminum concentration above 40% does not show such behavior.

It is well known that the reactions to form iron aluminides from pure Fe and Al powders are exothermic, which is a great concern due to the uncontrollable nature of the process. To solve this problem, several researchers have directed their investigations on the promising method called Self-propagating High-temperature Synthesis (SHS) [17-20]. The process enables to obtain FeAl hardened with Fe$_2$Al$_5$ and FeAl$_2$ inclusions, avoiding the tendency toward hydrogen embrittlement when being sprayed onto a substrate.

When dealing with bulk intermetallics, it has been observed that when FeAl contains solute additions (Cr, Mo), second phase or precipitates (Nb, Zr, C, B) the strength can be improved over 1,000 MPa. The drawback of poor creep resistance, a characteristic of iron aluminides, is caused by the ease movement of dislocations in the open bcc lattice. This can also be improved by stable particles such as carbides, dispersion boride particles or oxides formed in mechanically alloyed materials [20,21]. Table 6 shows the influence of some alloying elements on FeAl intermetallic properties [22]. One of the most frequently studied iron aluminide compositions is Fe-40Al (at.%), which corresponds to the zone of the FeAl intermetallic according to the phases diagram. Some investigations show comparisons between the performance of this compound both at high temperatures and at room temperature [23] reporting that surface hardness of bulk FeAl is observed to be higher at elevated temperatures owing to the formation of the Al$_2$O$_3$ and Fe$_2$O$_3$ layer. However, the elastic modulus decreases with temperature, which is also related to that amorphous oxide layer on the single crystal surface.

Mechanical tests and microstructure studies were also carried out on materials obtained by different processing and annealing procedures from milling pre-alloyed powders

Table 5 – The main special points of the Fe-Al system [15].

Reaction	Composition, at.% Ni			Temperature, °C	Reaction type
L + FeAl ↔ ε	60	52	~58	1,232	Peritectic
L + ε ↔ Fe$_2$Al$_5$	68.5	~70.5	~64.5	1,165	Eutectic
L ↔ Fe$_2$Al$_5$ + FeAl$_3$	~75	~72	~75	~1,160	Unknown
L ↔ FeAl$_3$ + (Al)	99.1	76.6	99.97	655	Eutectic
ε + Fe$_2$Al$_5$ ↔ FeAl$_2$	~65	~70	~66.5	1,156	Peritectoid
ε ↔ FeAl + FeAl$_2$	~71	~55	~66	1,102	Eutectoid
L ↔ Fe$_2$Al$_5$		71		1,169	Congruent
(αFe) ↔ FeAl		23.3		660	Tricritical
L ↔ δFe		0		1,538	Melting
L ↔ Al		100		660.452	Melting
δFe ↔ γFe		0		1,394	Allotropic
γFe ↔ αFe		0		912	Allotropic
Metastable					
L ↔ (Ni) + AlNi$_3$	98.3	85.7	~99.97	649	Eutectic

Table 6 – Effects of alloying elements on FeAl intermetallics characteristics [22].

Element	Alloying effect
Cr	Decreases strength and ductility by increasing tendency for intergranular fracture
B	Small addition (< 30 ppm) reinforces grain boundaries and increases ductility. Above this level, B is detrimental to ductility
Y	Decreases grain size
Zr	Increases ductility and reduces effect of impurities
Ce	Decreases grain size and controls grain growth at high temperatures

of nominal composition Fe-40Al-0.05Zr-50 ppm B with 1 wt% of Y_2O_3 [24]. B addition helps to remove carbon impurities as well as to improve room temperature ductility and fracture toughness. Y_2O_3 is introduced as fine dispersed particles by the mechanical alloying process, which helps to reinforce grain boundaries [3,25]. They show a variety of grain and particle sizes, which lead to oxide dispersion-strengthened compounds with interesting properties such as high strength with good tensile ductility for an intermetallic. The same authors have also collected information made available over the last years about FeAl, highlighting research about its ductility and creep resistance [26].

As previously mentioned, it is also important to understand intermetallics' creep behavior. For this purpose, a recent study has started from a base FeAl alloy (Fe-40Al-0.2Mo-0.05Zr-0.5Ti-0.2C-0.02B) whose properties have been compared to 2 other alloys: high carbon alloy (Fe-40Al-0.2Mo-0.05Zr-0.5Ti-0.7C-0.02B) and high transition metals alloy (Fe-40Al-0.5Mo-0.1Zr-1.0Ti-0.2C-0.02B) [8]. According to that study, the first one (solid solution hardened) exhibits the lowest creep rates, both at high and low stresses (3 orders of magnitude lower than those of the base alloy), whereas the second one (precipitation hardened) also shows lower creep rates than the base alloy and a correctly developed steady-state in the curve of creep strain versus time.

Over the last decade, it has been worth obtaining fine-grain particles so that ductility improves and, according to the Hall-Petch effect, so the materials would show an increase in hardness and strength. That is why an effort has been made to obtain nanocrystalline FeAl powders by several methods such as laser vaporization followed by controlled condensation (LVCC) [27], where an average particle size of 6-10 nm can be reached. The nano particles generated appear to be highly charged and aggregated into an organized porous structure, which could be promising in the areas of catalysis and filtration.

The nanocrystalline structure was also obtained as a coating by high velocity oxygen fuel (HVOF) [28] spraying milled powders of Fe-40 Al- 0.05 Zr- 50 ppm B with 1 wt% of Y_2O_3, atomized under argon atmosphere [21]. This article includes the effect of reducing the grain size and having boron in the intermetallic; it was foreseen that both factors would influence ductility. A more recent study by the same authors compares the hardness and porosity of the as-atomized and milled powders-obtained coatings [29]. The microstructural observation shows analogous characteristics (good density and adherence to the substrate) for both types. The nanostructured coating obtained by milling powder, which presented a disordered FeAl phase, was 35% harder than the conventional one (micrometer grain size) containing well-ordered FeAl and Fe_3Al phases. Another project by the same authors compared the microstructure and hardness of FeAl coatings with various thicknesses: 2 nanostructured deposits (5 mm and 300 μm) obtained by spraying milled Fe-40Al powder and a 5 mm microstructured deposit produced by APS from atomized powder and the initial feedstock powders [30]. It was observed that the HVOF of both the nanostructured deposits, 5 mm and 300 μm thick, showed a similar microstructure with the typical partially melted particles, but the thicker one accumulated more stresses in the region over 2 mm. Another conclusion

was that APS was effective in spraying atomized powder to high thickness, while HVOF was not.

The effectiveness of using HVOF in order to obtain adherent coatings with low or no porosity and oxide contents was also investigated for the composition of Fe-24.1Al-0.5Mo-0.1Zr (wt%, which means ~40Al at.%) by Totemeier et al. [31]. In this case, FeAl powders were prepared either by gas atomization alone or by gas atomization followed by ball milling to induce the desired nanocrystalline structure. A typical microstructure of such coating is shown in Fig. 2. The obtained results show coatings with beneficial compressive stresses and improvements in terms of hardness and resistance to tensile cracking by increasing particle velocities.

Iron aluminide coatings have also been produced by high velocity arc spraying (HVAS) [32]. This thermal spray technique provides higher adhesion strength and microhardness, lower density and porosity as well as excellent elevated temperature erosion resistance. The nominal composition was Fe-20.0Al-14.1O (at.%) and it led to coatings with a mixture of Fe_3Al, FeAl and α-Fe regions with fine alumina layers that exhibited low friction coefficients and low wear rate at high temperatures [19].

The SHS technique described above has also been studied to produce iron and nickel-aluminide powders reinforced with hard particles such as alumina, Cr and Ti carbides [21]. These powders were afterwards sprayed onto steel substrates [32] through air plasma spraying (APS) [33] and Gas Detonation Spraying (D-gun) [34]. Such coatings show better wear behavior, and good adhesion and thermal conductivity. In general, the Fe and Ni based powders contain low porosity, but the iron-based powders exhibit an inhomogeneous structure; the nickel-based powders appear to be homogeneous. Comparing the two thermal spraying methods, D-gun, which produces a very high velocity of particles impacting on the substrate, provides coatings with higher density than APS. While Ni-based powders show better bond strengths, Fe-based powders show better wear resistance results. Other relevant studies conducted recently center on diffusion behavior, which
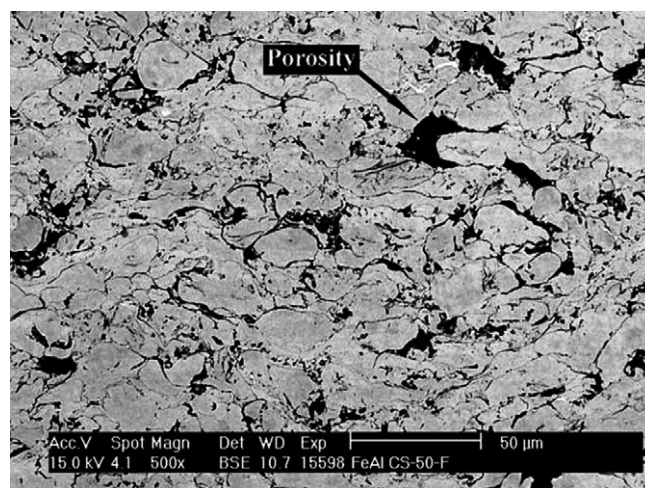
Fig. 2 – Typical microstructure of a FeAl coating high velocity oxygen fuel sprayed at a 540 m/s particle velocity (500×) [27].

appears to be interesting because of the peculiar structural defects, found in intermetallics with an ordered B2 crystal lattice (NiAl, CoAl, FeAl) [35].

2.2. NiTi intermetallics

NiTi, one of the equilibrium intermetallic phases in the Ni-Ti system, is interesting because it has two different crystal structures, depending on the temperature due to a martensitic-type transformation. This transformation leads to a shape memory effect. The high temperature 'austenitic' phase has a B2 (CsCl) structure, while the low temperature 'martensite' has a more complex monoclinic B-19'-type structure.

In general, the properties of titanium-based intermetallic alloys are: excellent high temperature mechanical properties; significantly lower density in comparison to superalloys; good creep resistance up to 1,000 °C; and oxidation resistance up to 900 °C.

Possible industrial applications are: turbocharger rotor, piston head for diesel engines, jet engine compressor rotor, high pressure turbine stator, turbine blades, and vane support rings. Special NiTi applications could be the following: as endovascular stents, vena cava filters, and dental files [36,37]; as actuators, temperature controllers, safety gears in household appliances, and radiators [38]; and in railroad wheel, or as contact tires on railroad wheels [36]. Table 7 shows relevant information about the Ni-Ti system and its characteristic reactions.

Titanium and its alloys are well known for their great erosion resistance, which are superior to that of stainless steel; that is why applying this material as a coating is an effective method for preventing erosion. Furthermore, their lower elastic modulus has made them a viable option for medical applications. Interestingly, the success of the intermetallic NiTi (often called Nitinol, due to its discovery in the Nickel Titanium Naval Ordnance Laboratory) comes from its well-known properties of thermal shape memory effect and mechanical shape memory effect or superelasticity (Fig. 3); thus, it has been studied extensively as a biomaterial since it was discovered in 1962 by Buechler [39].

Slightly nickel rich alloys present this effect known as 'superelasticity'. Both thermal and mechanical natures of shape memory are based on a solid-state phase change (martensite/austenite). The temperatures at which each of these phases begins and finishes forming are represented by the variables Ms, Mf, As and Af in Fig. 3. In the thermal shape memory effect, after obtaining martensite by cooling below Mf, it is deformed and heated to above Af so that the initial shape can be recovered.

On the other hand, as Ms, Mf, As and Af variables increase linearly with the amount of loading applied to the piece, the superelasticity consists of starting from a temperature above Af and, without change in temperature, increasing the load until martensite stress-induced structure appears. By removing the load, austenite can be recovered. These parameters have been characterized in a work by Itin et al. [40,41].

The reversible transformation martensite-austenite takes place in the temperature range from 50-100 °C depending on the concentration of Ni. A variation of the Ni contents by 0.1 at.% changes the transformation temperature by approximately 10 °C. It must be also pointed out that NiTi alloys should contain as few impurities (oxygen, carbon and nitrogen) as possible because the transformation temperatures are very sensitive to such impurities [37].
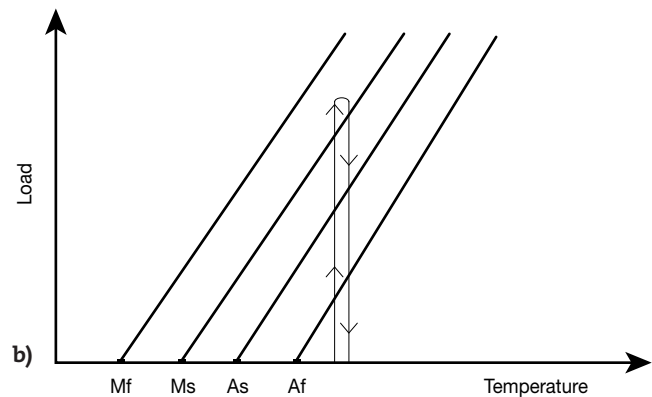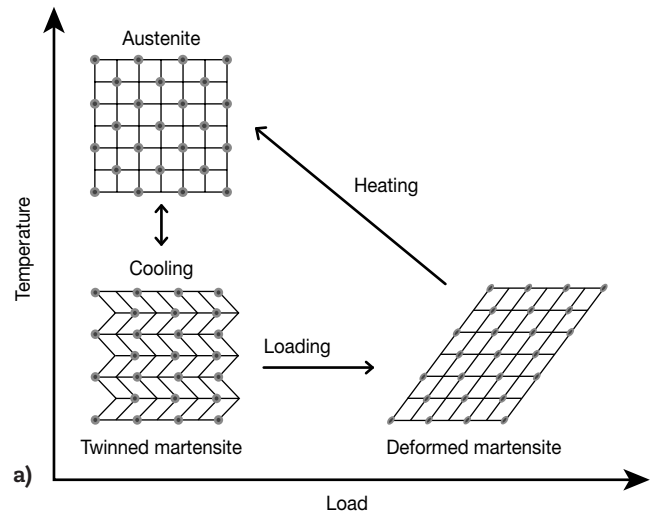
Fig. 3 – Shape Memory of NiTi. (a) Thermal shape memory effect. (b) Mechanical shape memory effect.

Table 7 – The main special points of the Ti-Ni system.					
Reaction	Composition, at.% Ni			Temperature, °C	Reaction type
L ↔ (βTi) + Ti$_2$Ni	24	10	33.3	942	Eutectic
L + TiNi ↔ Ti$_2$Ni	32	49.5	33.3	984	Peritectic
L ↔ TiNi + TiNi$_3$	61	57	75	1,118	Eutectic
L ↔ TiNi$_3$ + (Ni)	83.5	75	86.3	1,304	Eutectic
(βTi) ↔ (αTi) + Ti$_2$Ni	4.5	0.2	33.3	765	Eutectoid
TiNi ↔ Ti$_2$Ni + TiNi$_3$	49.5	33.3	75	630	Eutectoid
L ↔ TiNi		50		1,310	Congruent
L ↔ TiNi$_3$		75		1,380	Congruent
L ↔ Ni		100		1,455	Melting
L ↔ βTi		0		1,670	Melting
L ↔ (Ni) + AlNi$_3$		0		880	Allotropic

Another important aspect is its stress-strain behavior. Unlike conventional materials, after the first linear deformation when the load is applied, the stress remains approximately constant with strain and, during unloading, the deformation is removed with another constant range. Fig. 4 shows such behavior compared to stainless steel. NiTi exhibits elasticity over 10% compared to the near 1% that stainless steel can perform.

Several investigations outline its wear and corrosion resistance [39,42]. The corrosion performance is the key to deciding the biocompatibility of the material and it depends on the surface properties such as chemical composition, crystallinity and heterogeneity, roughness and wettability. The study of this performance denotes that Nitinol's corrosion resistance can compete with pure titanium or it can also be as poor as that of stainless steel [39]. This research also provides different possibilities for nitinol surface treatments. Some investigations with NiTi have also stated that the presence of an adherent TiO_2 surface oxide can prevent nickel dissolution [37]. Moving to its wear properties, Imbeny et al. carried out several micro-scale abrasion tests to decide how different abrasives affect nitinol behavior [36]. Another technique called Laser Surface Melting has also been investigated as a solution to improve corrosion resistance of NiTi plates [43]. Extreme caution is taken into this aspect, as the corrosion of high nickel surface content leads to allergic, toxic or carcinogenic effects.

The porosity of nitinol has also been investigated due to its fixation capability and tissue ingrowth when employed as an implant resource [38]. Actually, NiTi was first applied for orthodontic treatments followed by bone plates and, gradually, this intermetallic is being considered for more applications.

Moving on to the formation of NiTi compounds, some methods to produce this material for shape memory effect are based on the synthesis of the alloy starting from pure elemental metals by either vacuum induction melting (VIM) or vacuum arc remelting (VAR), and, afterwards, by hot working and forming to obtain the final desired shape. An alternative could be powder metallurgy processing from prealloyed metal powders or elemental powders because it prevents some problems related to machining operations; however, it
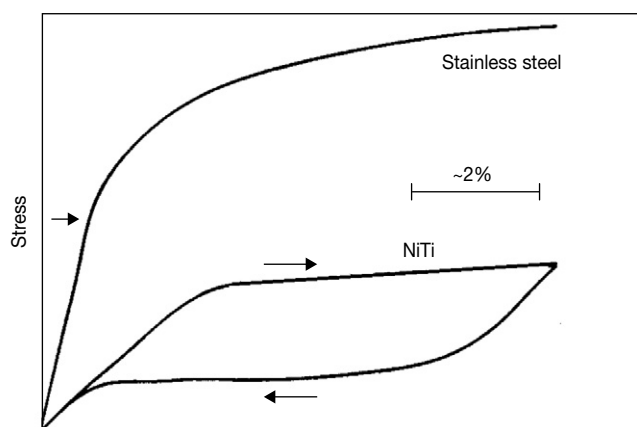
raises some inconveniences such as the formation of other phases, and the difficulty of obtaining high relative density or eliminating porosity [37,44]. Therefore, some powder synthesis routes to obtain NiTi are presented: a) reactive sintering; b) explosive shock synthesis; c) hot-isostatic pressing; d) hot-extruding; e) metal injection molding; f) self-propagation high temperature/combustion synthesis; g) vacuum plasma spraying; h) and laser plasma spraying.

As with the Fe-Al system, here, the already known Self Propagating High-Temperature Synthesis (SHS) technique is employed; in this case, preheating is necessary owing to the low exothermic character of the reactions between Ti and Ni during the process [45]. The SHS leads to the formation of TiNi, Ti2Ni, Ni3Ti and Ni4Ti3 intermetallics.

Apart from the widely discussed strong properties of nitinol, the high costs for manufacturing large NiTi components and their manufacturing challenges [46-48] present restraints. Therefore, this intermetallic has also been proposed as a coating material. In the early 1990s, several thermal spray techniques were used to obtain such coatings but unfortunately they did not fulfill adherence and integrity requirements [49]. However, recent studies using vacuum plasma spraying (VPS), requiring the spraying of elemental powder [50] with a nominal composition NiTi (50.8 at.% Ni), have obtained fairly reasonable results. Fig. 5 shows the cross sections of the NiTi coatings using different parameter sets described in Table 8.

Siegmann et al. [51] have also reviewed the properties of NiTi coatings obtained by VPS to avoid reactions with oxygen and nitrogen. It was observed that the principal phases persisted during the powder and coating production phases. A following study investigated VPS as well as low-pressure wire arc (LPWAS) applied for producing free-standing shape memory foils [52]. The second method, LPWAS, has proven to be successful in forming martensitic NiTi alloys that exhibit excellent thermal shape memory effects, while VPS spray-formed foils have presented problems in their superelastic behavior. The results with universal hardness testing showed that VPS sprayed austenitic NiTi material exhibit higher ductility within thin discrete layers of the foils than LPWAS-sprayed foil material.

In contrast, other investigations support that it is not possible to alloy a simple mixture of powders by VPS and mechanical alloying before spraying is needed in order to ensure and help alloying (50:50 and 40:60 at.% ratios were evaluated) [53]. The same study resorts to LPHS (*Laser Plasma Hybrid Spraying)* to synthesize NiTi coatings from pure Ni and Ti powders. The coatings obtained with this method [54] as well as with explosive welding [55] have been investigated for their cavitation erosion characteristics. Unlike explosive welding which needs heat treatment after the process, especially austenitic NiTi, coatings obtained by LPHS do not. Hiraga et al. [54] have demonstrated that cavitation properties are dependent on the laser irradiation parameters and comparing the mass loss rate among VPS and LPHS NiTi coatings (Ti-Ni 50 at.% mixed powder) and Ti6Al4V substrate, they found a better performance for LPHS NiTi coatings. Furthermore, with increased Ni content, erosion resistance improves too, because Ni is responsible for the decrease in the transformation temperature from austenite to martensite.
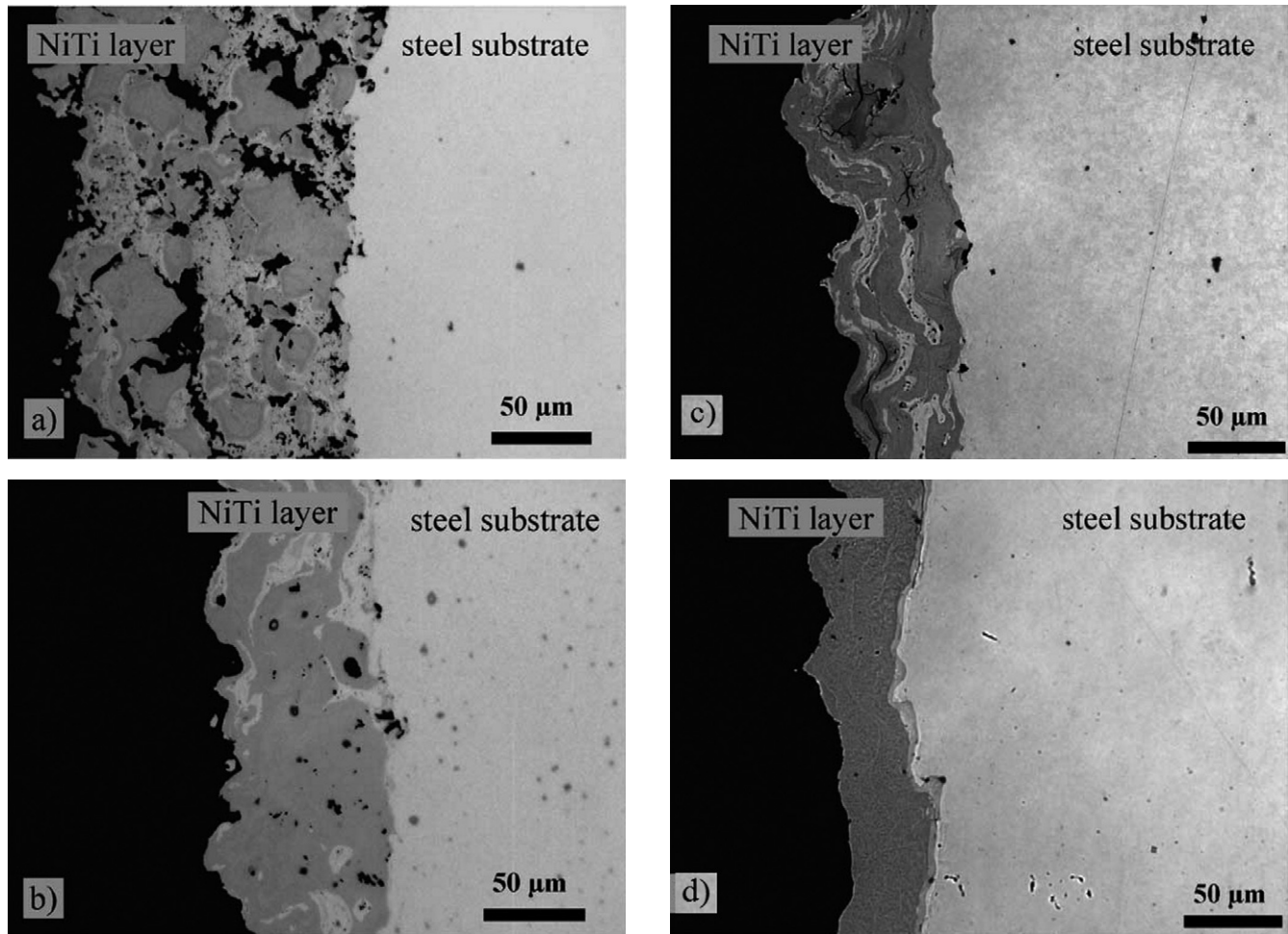

Fig. 4 – Stress-strain diagram for Nitinol and stainless steel: left arrow indicates elastic limit in stainless steel.

Fig. 5 – NiTi coatings on a steel substrate produced by vacuum plasma spraying with different parameter set [50].
(a) As-sprayed with parameter set 1; (b) as-sprayed with parameter set 2; (c) as-sprayed with parameter set 3;
(d) annealed at 900 °C, 2 hours. No differences observed compared to parameter set 4.

Table 8 – Parameter sets used for vacuum plasma spraying of NiTi coatings [50].

	Current (A)	Performance (kW)	Ar (L/min)	H_2 (L/min)	He (L/min)	Stand off distance (mm)	Substrate temperature (°C)
Set 1	800	55	50	0	30	250	700
Set 2	750	55	50	4	20	250	800
Set 3	740	55	50	6	8	250	800
Set 4	710	55	50	9	0	250	850

The suitability of laser use for remelting and finally forming the intermetallic has also been demonstrated by Wilden and Frank [56] for other systems such as Ti-Al and Al-Ni. As far as NiTi is concerned, the compositions investigated were 38Ni-62Ti, 27Ni-73Ti and 38Ni-62Ti at.%. Moreover, it includes how laser parameters affect the structurally resulting properties, such as microhardness and wear behavior. Apart from the several attempts made with sputtering, thermal spray techniques and explosive welding, a new successful method has been used to obtain thin NiTi films with higher adhesion and density: Cathodic Arc Plasma ion plating (CAP). It allows

scientists to prepare highly crystalline NiTi films without external heating and posting heat treatment. Unlike chemical composition, which is not dependent upon the substrate bias voltage, the crystallinity shows a strong dependence [50].

2.3. NiAl intermetallics

Ni$_3$Al has an L1$_2$ (cP4) crystal structure, a derivative of the fcc crystal structure. This unit cell contains 4 atoms. The Ni atoms occupy face-centered positions and the aluminum

occupies the corners of the unit cell. On the contrary, NiAl presents the same crystal structure as FeAl, B2 (cP2). The heat of formation and aluminum percentages of NiAl intermetallics are presented in Table 9.

In general, the properties of nickel-based intermetallic alloys are: resistance to oxidation and carburisation atmosphere; fatigue resistance superior to that of nickel based superalloys; excellent wear resistance at high temperature; and good tensile and compressive yield strength at 650-1,100 °C. Table 10 shows relevant information about the Ni-Al system and its characteristic reactions. Possible industrial applications are: transfer rolls, heat treating trays, centrifugally cast tubes, rails for walking beam furnaces, die blocks, nuts and bolts, corrosion resistance tool bits, single crystal turbine blades, aircraft fasteners, automotive turbochargers, pistons and valves, bellows for expansions joints to be used in corrosive environments and permanent molds.

Ni_3Al shows an increase of its elastic moduli, when temperatures reach a maximum between 600-800 °C, depending on small additions of alloying elements, as showed in Fig. 6. Similar to FeAl, it also forms an alumina layer that is responsible for its corrosion resistance.

Like other intermetallics, Ni_3Al exhibits hydrogen embrittlement and grain boundary fracture, especially in its polycrystalline form. This mode of fracture has been attributed to the interaction of the material with water vapor, especially at elevated temperatures, where Al_2O_3 film appears to be insufficient to prevent rapid intergranular crack propagation. The addition of Cr and the production of an elongated grain structure could ameliorate the problem at intermediate temperatures by reducing the oxygen penetration. At room temperature, the source of the intergranular fracture is weak grain boundaries, rather than environmental effects [11].

Deevi and Sikka [3] have discussed the previous work of Liu et al., showing that the addition of 0.5 at.% B in Ni_3Al resulted in a room-temperature tensile ductility of 50% at 24 at.%. The mechanical properties of several alloys were evaluated. Boron has been demonstrated to improve the ductility by changing the fracture from intergranular to transgranular. Its low creep resistance appears to be another obstacle for its use, however, instead of superalloys. Hafnium and zirconium are proven to be effective [3,11]. Furthermore, regarding grain size sensitivity, coarse grain materials show better creep properties.

Looking at NiAl properties, it appears to be more feasible for high-temperature applications than Ni_3Al. Nevertheless, poor ductility will be always a matter of concern at room temperature. Here, the major cause would be lack of sufficient slip systems. Surprisingly, decrease in grain size does not result in better ductility behavior of NiAl [11]. Boron added to NiAl serves as a potential solid-solution strengthener rather than as an effective suppressor of intergranular fracture.

In recent years, the formation of Ni_3Al as a surface medium has been studied by the magnetron sputtering technique and, subsequently, pulsed laser application [57]. Such studies show that higher laser intensity facilitates intermetallic formation.

NiAl presents high elastic moduli, and its high solubility for other alloying elements allows a notable oxidation resistance. An interesting study describes and analyses two methods to obtain NiAl powders that start from mechanical alloying Ni

Table 9 – Weight percentages of aluminum and heats of formation of FeAl intermetallics [5].

Intermetallic	Weight percent (wt%) of Al	Heat of formation, ΔH_{298} (kcal/mol)
Ni_3Al	13.28	−66.6 ± 1.2
NiAl	31.49	−28.3 ± 1.2
Ni_2Al_3	40.81	−67.5 ± 4.0
$NiAl_3$	57.96	−36.0 ± 2.0

Table 10 – The main special points of de Al-Ni system.

Reaction	Composition, at.% Ni			Temperature, °C	Reaction type
$L \leftrightarrow Al_3Ni + (Al)$	2.7	25.0	0.01	639.9	Eutectic
$L + Al_3Ni_2 \leftrightarrow Al_3Ni$	15.0	36.8	25.00	854.0	Peritectic
$L + AlNi \leftrightarrow Al_3Ni_2$	26.9	42.0	40.00	1,133.0	Peritectic
$AlNi + AlNi_3 \leftrightarrow Al_3Ni_5$	60.5	73.0	66.00	700.0	Peritectoid
$L + AlNi \leftrightarrow AlNi_3$	74.5	69.2	73.75	1,395.0	Peritectic
$L \leftrightarrow (Ni) + AlNi_3$	75.0	79.8	74.00	1,385.0	Eutectic
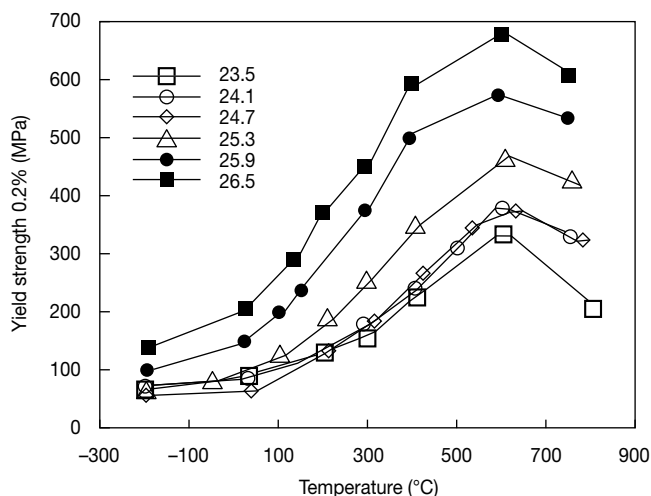
Fig. 6 – Ni_3Al elastic modulus dependence on the temperature for different Al content [3].

and Al powders. Whereas in the first one the mixture reacts gradually and exothermically over a long period of continuous milling, in the latter method, the intermetallic formation occurs by opening the milling vessel after a short period of milling [58].

It is also known, among other applications, the suitability of Ni-Al system for bond coating, specially the composition Ni-5wt%Al. In a study by Deshpande et al. [59] these powders have been sprayed through Air Plasma Spray in air (APS), Wire Arc spray, HVOF, and cold spray [60] (a very recent thermal spray development where a combination of very high particle velocity and low temperature is accomplished to produce coatings with very low porosity and oxide content) and the

obtained results have been discussed. Thus, properties such as adhesive/cohesive strength, porosity and oxides contents, and shape of grains were compared revealing in very dense and lower oxide content for those coatings sprayed by HVOF and cold spray (Fig. 7). HVOF is also used by Wang et al. [61,62] to form NiAl layers with Cr and CeO_2 additions, which improves the wetting and bond strength of the coatings to the substrate. This work also discusses hardness, elastic modulus and erosion resistance of such coatings, whit the authors concluding that coatings containing CeO_2 and Cr exhibit a significant increase in erosion resistance and a reduced tendency for brittle peeling, compared to pure NiAl coatings.

The erosion properties and thermal shock resistance have also been investigated for $NiAl-Al_2O_3$ HVOF coatings comparing to those of other cermet coatings produced with the same thermal spray technique [63]. The carbide cermet coatings showed variations of their erosion behavior with temperature, while $NiAl-40Al_2O_3$ coatings demonstrated less sensitivity. With respect to the effect of impact angle, high values were found to be favorable for the erosion-corrosion properties of the intermetallic/aluminium oxide coating.

In addition, several tests have been carried out to NiAl coatings obtained by HVOF to compare them with other hard materials deposited with the same thermal spray technique, mainly due to NiAl wear behavior in high pressure valves [64]. Process parameters and optimization in NiAl coatings produced by HVOF have been studied by Hearley et al. [65] to obtain promising coatings for applications in high-temperature corrosive environments. The best parameter set was proven to be: higher oxygen to fuel ratio equivalent to 80% stoichometry, a spherical inert gas atomized powder with a narrow particle size range between 15 μm to 45 μm, and a small percentage of particles > 50 μm.

3. Final remarks

As previously mentioned, other intermetallic alloys have been investigated in the recent past but not discussed in this work, such as TiAl and MoSi based alloys. A good reference for their study can be found in works by Yamaguchi et al. [66] and Vasudevan & Petrovic [67], to name a few.

As we pointed out, intermetallics continue to be a current challenging issue in the field of material science. Improvements in creep, fatigue and wear performance seems to be one of the main areas of research, especially dealing
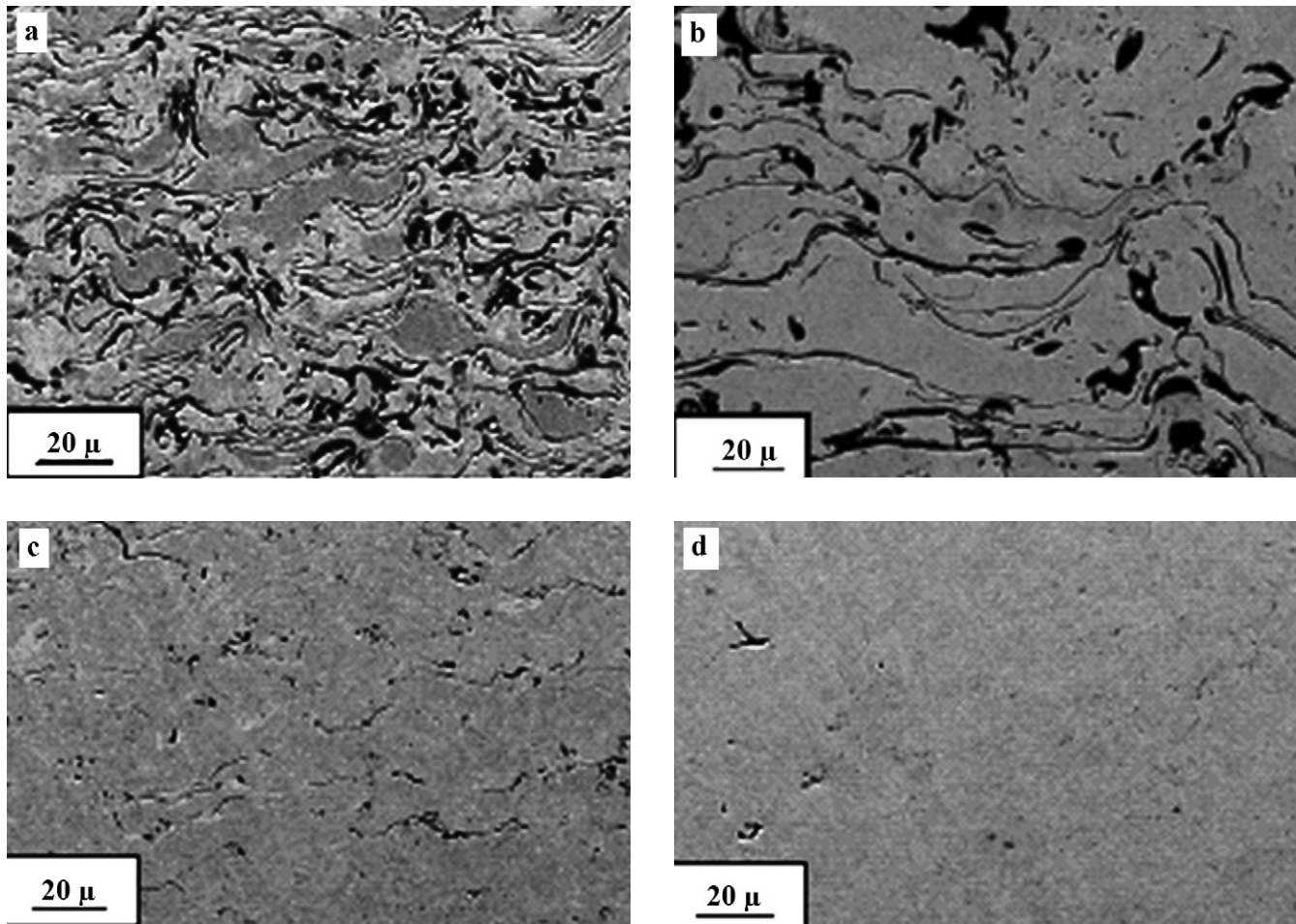
Fig. 7 – Ni5wt%Al coatings obtained by different thermal spray techniques [54]. (a) Wire arc; (b) APS; (c) high velocity oxygen fuel; (d) cold spray.

with room temperature properties. Specific studies involving interdisciplinary collaboration are growing more popular, as experts seek applications in areas such as biomedical engineering, nanoscience and information technology.

Especially for thermal spray technology, there are several important aspects of intermetallics application to be researched in order to better understand coatings behavior at room temperature and at high temperatures. Oxidation resistance is one of the most important characteristics that intermetallics should exhibit to be useful for high temperature applications. Therefore, it is conveniently high in Al, Cr or Si content. Since NiAl has been one of the widely used bond coat systems, scientists continue to study it to obtain improved results for new working environments or service conditions. In this perspective, FeAl and TiAl appear to be good options although few coating-related studies have been done for the latter.

Considering the improvement of properties shown to occur by reducing grain size, forthcoming studies should explore nanometer grain structures obtained by several thermal spray techniques. HVOF has been fairly studied for FeAl but the plasma technique, for instance, or even cold spray does not. Finally, it would be worth investigating nitinol, whose immediate applications are related to medicine. For this purpose, its surface properties are of particular importance, especially the issue of whether it is biocompatible.

Acknowledgments

R E F E R E N C E S

[1] Kurnakov NS, Zemczuzny SF, Zasedatelev M. J Inst Met. 1916;15:305.

[2] Aoki K, Izumi O. Flow and fracture behavior of Ni3 (Al-Ti) single crystals tested in tension. J Mater Sci. 1980;14:1800-6.

[3] Adeva P. Materiales alternativos de las superaleaciones: compuestos intermetálicos. Revista de la Asociación Española de Científicos. 1999;1:1-6.

[4] Tanaka R. Research and development of ultra-high temperature materials in Japan. Mat High Temp. 2000;17:457-64.

[5] Deevi SC, Sikka VK. Nickel and iron aluminides: an overview on properties, processing, and applications. Intermetallics. 1996;4:357-75.

[6] Schubert K. Kristallstrukturen zweikomponentiger Phasen. Berlin: Springer-Verlag; 1964.

[7] Frevel LK. A systematic classification of crystal structures. Acta Cryst. 1985;B41:304-10.

[8] Varin RA. Intermetallics: Crystal structures. In: Buschow KHJ, editor. Encyclopedia of materials: Science and technology. Oxford: Elsevier; 2001. p. 9913.

[9] Cahn RW. How does long-range order affect creep of alloys? Mater Sci Eng A. 2002;324:1-4.

[10] Cahn RW. Lattice parameter changes on disordering intermetallics. Intermetallics. 1999;7:1089-94.

[11] Liu CT, StieglerJO. Ordered Intermetallics. Properties and selection: nonferrous alloys and special purpose materials. Metals handbook. 10th ed. Ohio: ASM International; 1990.

[12] Zhang WJ, Sundar RS, Deevi SC. Improvement of the creep resistance of FeAl-based alloys. Intermetallics. 2004;12: 893-7.

[13] Arzt E, Behr R, Göhring E, Grahle P, Mason RP. Dispersion strengthening of intermetallics. Mater Sci Eng A. 1997;234-6: 22-9.

[14] Gschneider Jr. K, Russell A, Percharsky A. A family of ductile intermetallic compounds. Nat Mater. 2003;2:587-90.

[15] CD-ROM. Binary alloy phase diagrams. Version 1.0. 2nd ed. Plus Updates; 2006.

[16] Liu CT, George EP, Masiasz PJ, Schneibel JH. Recent advances in B2 iron aluminide alloys: deformation, fracture and alloy design. Mater Sci Eng A. 1998;258:84-98.

[17] Moore JJ, Feng HJ. Combustion synthesis of advanced materials: Part I and II. Prog Mater Sci. 1995;39:243.

[18] Ilyuschenko AP, Talako TL, Beliaev AV. Coatings of powders based on Iron aluminides. In: Lugscheider E, Berndt CC, editors. International Thermal Spray Conference. Essen, Germany; March 4-6, 2002. DVS Deutscher Verband für Schweißen, 2002. p. 1061.

[19] Sritharan T, Murali S, Hing P. Exothermic reactions in powder mixtures of Al, Fe and Si. Mater Lett. 2001;51:455-60.

[20] Bach FW, Babiak Z, Rothardt T. Properties of plasma and D-gun sprayed metal-matrix-composite (MMC) coatings based on ceramic hard particle reinforced Fe-, Ni-aluminide matrix. In: Marple BR, Moreau C, editors. Thermal spray 2003: Advancing the science and applying the technology. Orlando, FL; May 5-8, 2003. ASM International, 2003. p. 249-53. Vol. 1: p. 845; Vol. 2: p. 864.

[21] Morris DG, Muñoz-Morris MA, Chao J. Development of high strength, high ductility and high creep resistant iron aluminide. Intermetallics. 2004;12: 821-6.

[22] Testani C, Di Gianfrancesco A, Tassa O, Pocci D. FeAl intermetallics and applications: An overview. In: International Symposium on Nickel and Iron Aluminides: Processing, Properties and Applications. Proceedings from Materials Week 1996, Cincinnati, Ohio, S. 213-22.

[23] Xia J, Li CX, Dong H. Hot-stage nano-characterisations of an iron aluminide. Mater Sci Eng A. 2003;354:112-20.

[24] Muñoz-Morris MA, Garcia Oca C, Morris DG. Microstructure and room temperature strength of Fe-40Al containing nanocrystalline oxide particles. Acta Mater. 2003;51:5187-97.

[25] Grosdidier T, Tidu A, Liao H. Nanocrystalline Fe-40Al coating processed by thermal spraying of milled powder. Scripta Mater. 2001;44:387-93.

[26] Morris DG, Muñoz-Morris MA, Chao J. Development of high strength, high ductility and high creep resistant iron aluminide. Intermetallics. 2004;12:821-6.

[27] Pithawalla YB, Deevi SC, El-Shall MS. Preparation of ultrafine and nanocrystalline FeAl powders. Mater Sci Eng A. 2002; 329-331:92-8.

[28] Sobolev VV, Guilemany J, Nutting J. High velocity oxy-fuel spraying. London: Maney Publishing; 2004.

[29] Grosdidier T, Liao HL. X-rays and TEM characterization of nanocrystalline iron aluminide coatings prepared by HVOF thermal spraying. In: Lugscheider E, Berndt CC. International Thermal Spray Conference. Essen, Germany; March 4-6, 2002. DVS Deutscher Verband für Schweißen, 2002. p. 1061.

[30] Ji G, Grosdidier T, Liao HL, Morniroli JP, Coddet C. Spray forming thick nanostructured and microstructured FeAl deposits. Intermetallics. 2005;13:596-607.

[31] Totemeier TC, Wright RN, Swank WD. FeAl and Mo-Si-B intermetallic coatings prepared by thermal spraying. Intermetallics. 2004;12:1335-44.

[32] Bin-shi X, Zi-xin Z, Wei Z, Shi-ning M. The microstructure and high temperature sliding wear behavior of Fe-Al coating produced by HVAS. In: Thermal spray 2004: Advances in technology and application. ASM International, Osaka, Japan; May 10-12, 2004. ASM International 2004. p. 19-22, 1129 p.

[33] Suryanarayanan P. Plasma spraying. Theory and applications. Singapore: World Scientific Publishing; 1994.

[34] Pawlowski L. The science and engineering of thermal spray coatings. New York: John Wiley & Sons; 1995.

[35] Nakamura R, Takasawa K, Yamazaki Y, Ijima Y. Single-phase interdiffusion in the B2 type intermetallic compounds NiAl, CoAl and FeAl. Intermetallics. 2002;10:195-204.

[36] Imbeni V, Martini C, Prandstraller D, Poli G, Trepanier C, Duerig TW. Preliminary study of micro-scale abrasive wear of a NiTi shape memory alloy. Wear. 2003;254:1299-306.

[37] NAMAMET. UMR 5060 CNRS/UTBM, 2004.

[38] He JL, Won KW, Chang JT. TiNi thin films prepared by cathodic arc plasma ion plating. Thin Solid Films. 2000;359:46-54.

[39] Buechler W, Gilfrick J, Wiley R. Journal of applied physics. 1963;34:1475-7. *apud* Shabalovskaya SA. Physicochemical and biological aspects of nitinol as a biomaterial. Int Mater Review. 2001;46:41.

[40] Itin VI, Gyunter VE, Shabalovskaya SA, Sachdeva RLC. Mechanical properties and shape memory of porous nitinol. Mater Charact. 1994;32:179-87.

[41] Guilemany JM. The science and technology of shape memory alloys. Universitat de Barcelona – Universitat Illes Balears. Curso COMETT de la CEE. Barcelona, 1989.

[42] Shabalovskaya S, Rondelli G, Anderegg J, Xiong JP, Wu M. Comparative corrosion performance of black oxide, sand-blasted, and fine-drawn nitinol wires in potentiodynamic and potentiostatic tests: Effects of chemical etching and electropolishing. J Biomed Mater Res Part B: Applied Biomater. 2004;69B:223-31.

[43] Villermaux F, Tabrizian M, Yahia LH, Meunier M, Piron DL. Excimer laser treatment of NiTi shape memory alloy biomaterials. Appl Surf Sci. 1997;109-110:62-6.

[44] Locci AM, Orrù R, Cao G, Munir ZA. Field-activated pressure-assisted synthesis of NiTi. Intermetallics. 2003;11:555-71.

[45] Li BY, Rong LJ, Li YY. Fabrication of cellular NiTi intermetallic compounds. J Mater Res. 2000;15:10-3.

[46] Wu SK, Lin HC, Chen YC. A study on the machinability of a $Ti_{49.6}Ni_{50.4}$ shape memory alloy. Mater Lett. 1999;40:27-32.

[47] Lin HC, Lin KM, Chen YC. A study on the machining characteristics of TiNi shape memory alloys. J Mater Process Technol. 2000;105:327-32.

[48] Weinert K, Petzoldt V. Machining of NiTi based shape memory alloys. Mater Sci Eng A. 2004;378:180-4.

[49] Jardine AP, Field Y, Herman H, Marantz DR, Kowalsky KA. Processing and properties of arc-sprayed shape memory effect NiTi. Scr. Metall et Mater. 1990;24:2390-6.

[50] Bram M, Ahmad-Khanlou A, Buchkremer HP, Stöver D. Vacuum plasma spraying of NiTi protection layers. Mater Lett. 2002;57:647-51.

[51] Siegmann S, Halter K, Wielage B. Vacuum plasma sprayed coatings and freestanding parts of NiTi shape memory alloy. In: Lugscheider E, Berndt CC, editors. International Thermal Spray Conference. Essen, Germany; March 4-6, 2002. DVS Deutscher Verband für Schweißen, 2002. p. 1061.

[52] Halter K, Sickinger A, Zysset L, Siegmann S. low pressure wire arc and vacuum plasma spraying of NiTi shape memory alloys. In: Marple BR, Moreau C, editors. Thermal spray 2003: Advancing the science and applying the technology. Orlando, FL; May 5-8, 2003. ASM International; 2003. Vol. 1: 845 pp; Vol. 2, 864 p.

[53] Hiraga H, Inoue T, Kamado S, Kojima Y, Matsunawa A, Shimura H. Fabrication of NiTi intermetallic compound coating made by laser plasma hybrid spraying of mechanically alloyed powders. Surf Coat Technol. 2001;139:93-100.

[54] Hiraga H, Inoue T, Shimura H, Matsunawa A. Cavitation erosion mechanism of NiTi coatings made by laser plasma hybrid spraying. Wear .1999;231:272-8.

[55] Richman RH, Rao AS, Kung D. Cavitation erosion of NiTi explosively welded to steel. Wear. 1995 181-183:80-5.

[56] Wilden J, Frank H. Formation of intermetallic phases by laser alloying of thermally sprayed Ti and Al coatings for enhanced wear resistance of lightweight materials. In: Marple BR, Moreau C, editors. Thermal spray 2003: Advancing the science and applying the technology. Orlando, FL; May 5-8, 2003. ASM International; 2003. p. 475-83. Vol. 1: 845 p; Vol. 2, 864 p.

[57] Liu Z, Meng XK, Recktenwald T, Mücklich F. Patterned inter-metallic reaction of Ni3Al by laser interference. Mat Sci Eng A. 2003;342:101-3.

[58] Moshksar MM, Mirzaee M. Formation of NiAl intermetallic by gradual and explosive exothermic reaction mechanism during ball milling. Intermetallics. 2004;12:1361-6.

[59] Deshpande S, Sampath S, Gouma PI, Herman H. Micro-structural characterization across length scales of thermal sprayed Ni-5wt% Al coatings. In: Marple BR, Moreau C, editors. Thermal spray 2003: Advancing the science and applying the technology. Orlando, FL; May 5-8, 2003. Ohio: ASM International; 2003. p. 1475-1428. Vol. 1: 845 pp; Vol. 2, 864 p.

[60] Davis JR, editor. Handbook of thermal spray technology. Ohio: ASM International; 2004.

[61] Wang Y, Chen W, Wang L. Micro-indentation and erosion properties of thermal sprayed NiAl intermetallic-based alloy coatings. Wear. 2003;254:350-5.

[62] Wang Y, Chen W. Microstructures, properties and high-temperature carburisation resistances of HVOF thermal sprayed NiAl intermetallic-based alloy coatings. Surf Coat Technol. 2004;183:18-28.

[63] Wang B, Lee SW. Erosion-corrosion behavior of HVOF NiAl-Al_2O_3 intermetallic-ceramic coating. Wear. 2000;239:83-90.

[64] Scrivani A, Ianelli S, Rossi A, Groppetti R, Casadei F, Rizzi G. A contribution to the surface analysis and characterization of HVOF coatings for petrochemical application. Wear. 2001;250:107-13.

[65] Hearley JA, Little JA, Sturgeon AJ. The effect of spray parameters on the properties of high velocity oxy-fuel NiAl intermetallic coatings. Surf Coat Technol. 2000;123:210-8.

[66] Yamaguchi M, Inui H, Ito K. High temperature structural intermetallics. Acta Mater. 2000;48:307-22.

[67] Vasudevan AK, Petrovic JJ. A comparative overview of molybdenum disilicide composites. Mater Sci Eng A. 1992; 155:1-17.