Advanced materials for high temperature applications. New ways of elaboration

Jean-Claude GACHON

Laboratoire de Thermodynamique Métallurgique, ER 78,

Université de Nancy I, Faculté des Sciences, B.P. 239

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Abstract : New routes to prepare alloys from elements or preliminary compounds are described. Both mechanical alloying and thermally activated diffusion processes yield amorphous or crystalline alloys. The solid combustion synthesis which is one very interesting way to produce intermediate compounds is herein considered and new results are reported.

I - Introduction

The most classical way of producing alloys is to melt the metal components or ore with different additions. This method leads to a lot of drawbacks when some categories of alloys are considered. Superalloys are a good example of this. During melting of the elements, typically : Ni, Co, Cr, Mo, W, Al, Ti, Fe, ... all these metals have different melting points and densities, so it is necessary to reach such a temperature that those metals, like W or Mo, which do not melt at this temperature completely dissolve in the liquid. At the same time, it is necessary to ensure the homogeneity of the liquid and to avoid oxidation, especially of metals like Al or Zr which give very hard and stable oxides. The next step is solidification and then new difficulties arise. Segregations may occur, dendrites and interdendritic pores are encountered, and even cracks due to thermal stresses are observed. All these problems are solved in the classical elaboration of superalloys, by multiplying the number of melting, filtration of the liquid, refining ... to get a clean and homogeneous liquid alloy and by carefully controling solidification processes. To reduce the time cost of these routine fabrications new ways have been explored. Some of these non-conventional ways of alloy production will be described in the following pages.

II - Generalities about alternative routes

If melting of the components and solidification of the alloy are to be avoided, it is possible to envisage vapor-solid, liquid-solid or solid-solid reactions.

Processes involving both vapor and solid states, such as Physical Vapor Deposition (PVD) and Chemical Vapor Deposition (CVD), generally involve vapors which are not those of pure metals, especially for low vapor pressure metals, and their yields of solid are low. So they are used mainly to produce thin layers of materials, or nanometric powders. They will no longer be considered here. To produce bulk materials in industrial quantities, liquid-solid and solid-solid processes with sufficient yield are the most interesting. It is possible to divide them into two classes :

- thermally activated : slow diffusion processes and fast diffusion processes.
- mechanically activated : mechanical alloying.

For thermally activated processes, the distinction between "slow" and "fast" diffusion is arbitrary. A possible suggestion is that slow diffusion processes would be those which cannot be self accelerating, while fast diffusion processes would be those which are self-accelerating or very close to the conditions of self-acceleration. In such a case an endothermic reaction would always be considered as a "slow reaction", without consideration of the true diffusion rates of species, but this is not troublesome because an endothermic reaction is easy to keep under control while an exothermic reaction will often be self accelerating and not easy, even impossible, to control.

At first glance, it seems that mechanical alloying is completely separate from thermally induced reactions but :

i) when a mechanically induced reaction between metals is exothermic, as in the case of Ni + Zr for instance, the temperature of the powders may increase sharply and thermal diffusion may become the most important contribution to the formation of the alloy ;

ii) the thermal contribution through diffusion can only be totally neglected when metals of high melting points are treated. When metals with low melting points are mechanically alloyed noticeable diffusion may occur. In the case of lead or tin for instance diffusion is active at room temperature, and tin melting has been observed during mechanical alloying (1). In addition mechanical alloying and thermal treatments may be combined.

III - Mechanical alloying

It is not possible in a short space to completely review, all the results which were published in the literature. About six hundred papers have appeared on the subject since 1991, (2). Just a schematic overview will be given here.

III - 1 Principle of mechanical alloying

The essence of mechanical alloying is the fact that repeated violent impacts of hard bodies on mixed metal powders deform the grains, cold weld them one to the other and fragment them. The repetition of these events leads to new grains which are composed of thin layers of the initial components. Between these layers short distance interdiffusion occurs and amorphous or crystalline phases appear. After sufficient duration, a powder of the amorphous or crystalline compound is got. The size of the final grains is not influenced by the initial metal powder grains but depends on the mechanical alloying process itself.

III - 2 Typical results of mechanical alloying

The first point is that the mean temperature of the ball mill and the powders inside is generally low, so long distance interdiffusion is not active and amorphous alloys may be obtained from crystalline metal powders, at least when these metals have high melting temperatures, like transition metals. Estimations of the real temperature inside a grain during one impact has been made (3) and gave about 250°C, for a velocity of the balls of about 3.6 m.s^{-1} meaning around 30 m J of kinetic energy per ball. What is important to notice is that the ratio of the energy consumption due to the powder to that of the ball mill itself is very low. With a Fristch Pulverisette 07, power measurements gave, in sequence :

1	without vials		230 W
2	with 1 empty vial (760 g) 1 counterweight		238 W
3	with 1 counterweight 1 vial + 7 balls (96 grams)		248 W

4	with	1 counterweight	1 vial + 7 balls	
	+ 10 grams of iron powder Koch Light 8365 w, 99.5 %, at the beginning			254 W
	and after about 15-17 minutes			250 W - 249 W
5	with	1 counterweight	1 vial + 7 balls, powder removed	248-250 W
6	with	1 counterweight	1 empty vial	238 W

It can be seen that in this case the power which is absorbed by the powder is a few watts at the most, and after a quarter of an hour it is just 1 watt or less out of 250 (4). Such a decrease may be attributed to the hardening of the powder. So, such a low energy transfer to powders may explain why only short distance diffusion occurs and then why amorphous alloys, or cristalline compounds with small and simple unit cells are produced by M. A. (5).

Typical results which were reported are broad ranges of composition for amorphous transition metal alloys with enthalpies of formation of - 20 kJ per mole of atoms or more exothermic (27 to 83 at % Ni in Ni Zr (6), coupled with extended cristalline solid solutions (20 at % Ti in Ni or Fe (7). For Al and Mg, with lower melting points than that of the transition metals, crystalline phases were got (5) ; a supersaturated solid solution of Mg in Al and the γ phase with 58 atoms per unit cell. The β Al Mg phase probably didn't form because the diffusion distances were too short to allow the organization of a phase with more than 1000 atoms per unit cell.

III - 3 Extensions of mechanical alloying

Mechanical alloying involves solid particles which are smashed, cold welded, resmashed ... but a liquid or a reacting gas may be added to the solid powder, in view of modifying the process which otherwise generally takes place under an inert gas. For instance milling of Ni and Zr under N_2 led to a ternary nitride (8). Milling of Ni Zr crystalline powder with N_2 led to an amorphous ternary nitride, while with H_2 a crystalline hydride was formed.

It is also possible to reduce oxides by MA of a metal oxide and a more oxidable metal as a reducing agent. In this case, an inert liquid has to be introduced into the vial to control the rate of reduction (9)

IV - Slow diffusion processes

IV - 1 Solid-solid processes

Slow diffusion solid-solid processes for the elaboration of alloys have to be distinguished from the well know powder metallurgy processes which involve powders of the alloys. In this case alloys are generally classically prepared in the liquid state and atomized to avoid (i) solidification problems, (ii) workability problems. Nearly instanteneous solidification of small droplets avoids segregations, dendrites, and thermal cracks. Compaction is generally conducted in such a way that the final grains are not really bigger than those of the starting powders. Both thermal (by external heating) and mechanical contributions to consolidation are essential.

When an alloy is to be produced from elemental powders, the problem is not the same because diffusion takes place between different elements and heat may be produced by the alloying reaction. The heat production rate is a key factor for all the different methods which are used. Two kinds of alloys may be produced : primary solid solutions or intermetallic compounds. Primary solid solutions are the typical

products of slow diffusion processes because the enthalpies of formation of terminal solid solutions are generally such that they cannot dramatically modify the conditions of diffusion imposed by external heating.

For instance, the well know Ti-6Al-4V may be produced by blending powders of the components and diffusion alloying in the solid state (10). After blending to the desired bulk alloy composition, compaction is performed either by cold isostatic pressing (CIP) with a "soft" tooling or by mechanical pressing with hard tooling. Pressures which are used are up to 400 MPa and give green compacts of 85 to 90 % density. Then, these compacts are vacuum sintered at about 1260° to a density 95-99 %. At such a temperature pure Al is not yet solid, but during heating Al_3Ti and Al_3V may form as soon as Al melts. Both compounds have the same crystallographic structure (tI8, Al_3Ti type) and melt at around 1350°C. So, the formation of the definitive alloy is a solid-solid reaction. Full density is not achieved after sintering but additional hot isostatic pressing may be used. Near net shapes, preforms for forging, or foils may be produced by this method.

Slow diffusion yields also amorphous alloys between very thin layers of pure metals (11).

Production of intermetallic compounds may be envisaged by solid solid slow diffusion processes but the very exothermic enthalpies of formation of the compounds impose low sintering temperatures and therefore very long periods of treatment in order to avoid self-heating of the product and self-acceleration of the reaction. This feature makes solid-solid slow diffusion routes less interesting than fast diffusion processes.

IV - 2 Solid-liquid processes

Slow diffusion solid-liquid processes are those devoted to heavy alloys, the composites made of one refractory metal and another, or some others, with lower melting points, such as W and Cu for instance. W and Cu are non miscible elements, even at the melting point of W (12), but composites made of both metals are of interest because they combine a good thermal conductivity and a low thermal expansion coefficient (13). Powders of W (~90 wt %), Cu (~10 wg %) and a sintering activator (≤ 1 wt % Fe, Co, Ni or Pd) are mixed. Sintering is performed under dry H_2 at temperatures ranging from 1250°C to 1400°C. At those temperatures the third element dissolves W (like Ni or Pd) and is also soluble in Cu, or gives an intermediate compound with W ($Co_7 W_6$ or $Fe_7 W_6$) while having very limited solubility in Cu. The best formula to improve the final density and the mechanical properties is the formation of the intermediate compound $M_7 W_6$ in the form of thin layers around W grains to enhance sintering through a higher diffusion rate of W in the compound than in W itself. An optimum thickness of these layers (between 1 and 4 monolayers) is obtained with a concentration of 0.35 wt % of Co. The effect of Co in this case is such that at 1400°C Cu exudes from the compact pieces (13).

Another way to improve the mechanical properties of W heavy alloys is to separate W grains by thermal constraints. Joon-Wong Noth et al (14) report that a heavy alloy 93 wt % W - 5.6 wt % Ni - 1.4 wt % Fe prepared from powders of 2.5, 3 and 3.5 μm average size respectively and liquid sintered at 1485°C under H_2 for 1 hour may be mechanically improved by further heat treatment. The heat treatment consisted in isothermal holdings at 1150° under N_2 and water quenching between and after successive isothermal holdings. The total holding time at 1150°C was kept constant, 1 hour, whatever the number of water quenchings. A final density better than 99.7 % was always achieved. Increasing the number of water quenchings modified the contact between W grains, the higher the number of quenchings, the smaller the contact area between W grains. This led to a better penetration of the matrix between the grains and greatly

improved the impact energy of the heavy alloy (0 water quenching : 57 J, 20 water quenchings : 170 J) but not the tensile strength and the elongation.

Reactive infiltration of a solid Ni preform by liquid Al has also been studied (15). In these experiments the combination of Ni grains (and pores) sizes, pressure on the infiltrating liquid Al and temperature of the Ni preform, as well, as in some cases, presence of inert Al_2O_3 as heat sink or diffusion shield around Ni grains allow to adjust the ratio between diffusion and infiltration rates, but the process is very delicate to control. Infiltration must be quicker than reaction and this is in fact very close to fast diffusion processes.

V - Fast diffusion processes

These processes are those which involve exothermic reactions and which are able to self-propagate, or even self-accelerate. They are often termed "Solid Combustion Synthesis" (SCS) or "Self propagating High temperature Synthesis" (SHS).

V - 1 Fundamental of SHS

If a reaction $A_s + B_s = AB_s$ is exothermic and happens in adiabatic conditions, then the final temperature of AB is called its "adiabatic temperature" T_{ad}. If $\Delta_f H$ is the enthalpy of reaction it may be written, to define T_{ad}, as :

$$\Delta_f H\,(T_1) = \int_{T_1}^{T_{ad}} C_p\, dT$$

with T_1 the initial temperature of the elements and C_p the thermal capacity of the product :

If T_{ad} is greater than the melting point of the product

$$\Delta_f H\,(T_1) = \int_{T_1}^{T_m} C_{ps}^{(AB)}\, dT + \Delta H_{melting}^{(AB)} + \int_{T_m}^{T_{ad}} C_{pl}^{(AB)}\, dT$$

Generally T_1 is taken as 298 K (6). It has been empirically stated that a reaction may be self-sustaining if $T_{ad} \geq 1800$ K (7), which means that the possibility of self combustion depends on T_1, and on the heat dissipation during the process, since true adiabatic conditions are rarely achieved.

Combustion of a mixture of A and B starts at the hottest point of the system and, if the thermal conditions are favorable, propagates through all the sample. A homogeneous product is generally the result of a steady state of combustion. If thermal dissipation is too important and the reaction temperature too low, then the combustion may be perturbed and products are generally inhomogeneous. In the worst cases extinction is the sanction of misconducted reactions.

V - 2 Practical features of S.H.S.

Ignition

The simplest way of ignition is local heating of a powder compact when the enthalpy of reaction is exothermic enough to provoke a steady state reaction. When a steady state of combustion is difficult to obtain and to maintain, other ignition processes are possible, like chemical owen or thermal explosion (16). The chemical owen is a direct application of the SHS itself : the mixture of elements to be combined is completely surrounded by another mixture of highly reactive materials. The reaction inside the outer layer

of material gives a burst of heat to the inner part which reacts and adds its own heat to that of the owen. The final temperature in this case may be very high and a cast product is obtainable. The thermal explosion mode consists of heating the elemental blended powders at a constant rate until they react. The reaction is, as in the chemical owen, very quick and a cast product may be obtained (16, 18).

Properties of the products

Products are generally very porous because of i) the green density which is never 100 %, ii) of the volume reduction which accompanies the compound formation and iii) of phenomenae due to Kirkendall diffusion effects and capillary forces between solid and liquid phases (19). The most widely used of the porous products is powder production by grinding and subsequent sintering. The sinterability of SHS powders seems not really higher than that of other powders in spite of some claims (16). The homogeneity of the products depends on the process and its progress. One objective is to produce directly a compact homogeneous product by combustion. This supposes a reaction which leads to the liquid state at the reaction front in order to suppress porosity (16) but the time during which the liquid state has to be maintained has to be kept under control to avoid the problems encountered in classical metallurgy during solidification. The control of the combustion is a crucial problem in order to get good results.

V - 3 Control of the SHS process

Two levels may be envisaged :

- the first is the overall check of the combustion parameters : temperature of the components at the reaction front, cooling rate of products, propagation rate of the reaction,

- the second is closely watchting the structural changes during the reaction.

Controls belonging to the first level are relatively easy to perform, while it is more difficult to get a true insight of the structural transformations during the reaction. A complete reaction may occur within less than one second or within a few seconds. It is impossible to quench samples at different degrees of transformation. In-situ observation is necessary. This has already been carried out in a few cases. Pionners were J. Wong et al (20) who studied Ti + C = TiC, Ti + Ni =NiTi, Ti + Ni + C = TiNi + TiC and Al + Ni = AlNi. They used the high intensity X-ray beam provided by the Brookhaven National Synchroton in the U.S.A. to irradiate a compact of blended elemental powders and photodiode detectors to collect the scattered X-rays. With the help of some electronics and a P.C. it was possible to realise successive X-ray patterns within 30 to 100 milliseconds each and to store them. The combustion was initiated at one end of the compact and propagated through it while the X-ray beam irradiated the middle of the sample. It was then possible to "see" the temperature increase of the elements by their dilatation and to "see" and follow the reaction. One interesting point was the probable detection of a solid disordered Al Ni phase before the appearance of the Cs Cl structure. New results have been obtained in the USA (21) on Ta + C = TaC and 2Ta + C = Ta$_2$C and also in France on Ni + Zr = NiZr. The French results were got with the help of the LURE synchroton in Orsay. So, it is now possible to envisage a real "in situ" study of solid combustion phenomenae. Figure 1 shows what was obtained in France, concerning the reaction Ni + Zr = NiZr (22).

VI - Conclusion

It has been shown here that alloy production does not only rely on classical melting or smelting processes. It is now possible to produce alloys by methods which eliminate some drawbacks of the classical routes.
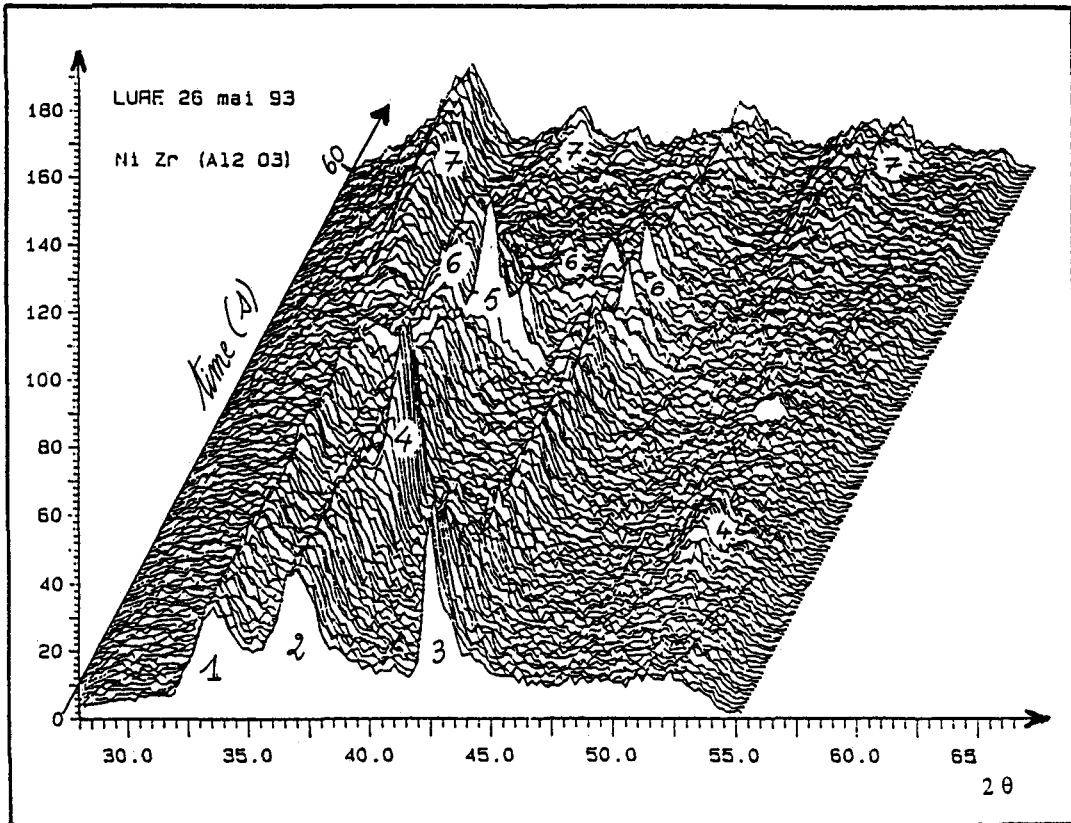
Fig 1　Reaction Ni + Zr = Ni Zr

　　　Moderator : Al_2O_3 powder, 50 % volume

　　　Each broken line represents the mean of 15 X-ray patterns of 30 ms each.

　　　1　$Zr\,H_2\,\varepsilon$

　　　2　$Zr\,H2\,\varepsilon + Zr\,\beta$

　　　3　$Ni\,(111)$

　　　4　NiZ_2 appears and melts (~ 1120°C)

　　　5　$Zr\,H_2\,\delta$

　　　6　$Ni\,Zr$ appears and melts (~ 1180°C)

　　　7　$Zr\,O_2\,\gamma$ forms after perforation of the mylar window of the reaction chamber previously kept under vacuum.

Mechanical alloying produces powders of crystalline or amorphous alloys as well as composites. It allows to perform some redox reactions at controled rates. Its drawback is the long time needed to get the final product. Diffusion between solids or solids and liquids is also capable of producing amorphous or crystalline alloys when starting from elements or preliminary compounds. SHS (or SCS) is a very interesting route with such advantages as cleaner products, rapidity, low energy consumption, possibility

of continuous processes but with such disadvantages as the need of synchrotron produced X-rays to get an insight into the combustion reactions, the porosity of most products and the impossibility of sustaining endothermic reactions. These latter reactions must be obtained by external heating but also have the advantage of being easy to keep under control.

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