

Mechanical alloying effects on the thermal behaviour of a Fe-Mn-Si-Cr-Ni shape memory alloy under powder form

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By means of simultaneous thermal analysis (STA), comprising differential scanning calorimetry (DSC) and thermal gravimetry (TG), a repetitive solid state transformation has been observed which was associated with Ni ferromagnetic-paramagnetic transition within the powders of an Fe-based shape memory alloy (SMA) with nominal composition Fe-14 Mn-6 Si-9 Cr-5 Ni (mass. %). During thermal cycling up to 773 K an obvious exothermic step on heating and an endothermic step on cooling were revealed on heat flow variation with temperature, the magnitude of which augmented with decreasing the temperature variation rate. The effects of mechanical alloying and thermal cycling on this magnetic transition were analysed both from calorimetric and structural point of view, by means of a DSC thermograph and a scanning electron microscope with focussed ion beam (SEM-FIB), respectively. The latter evidenced an obvious increase of oxygen level on the surface of Fe particles of thermally cycled powders which suggests the overlapping of an oxidation process on the magnetic transition, in accordance with the data obtained by TG.

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1. Introduction

Amongst shape memory alloys (SMAs) four systems have become of commercial use, based on: Ti-Ni, Cu-Zn-Al, Cu-Al-Ni and Fe-Mn-Si [1]. Due to their lower cost and superior technological properties (high plasticity, workability and weldability) [2] Fe-Mn-Si based SMAs seem to have the highest application potential even if they have been developed only under two commercial forms: Fe-28 Mn-6 Si-5 Cr [3] and Fe-14 Mn-5 Si-9 Cr-5 Ni [4] (mass. %, as all compositions will be listed hereinafter).

Ternary Fe-Mn-Si alloys are relatively easy to produce by classical conventional metallurgy (CM), based on melting, alloying and casting [5]. Conversely, quinary Fe-Mn-Si-Cr-Ni alloys are exposed to several technological CM drawbacks, such as compositional segregation, difficult incorporation of Si into melt, manganese loss on melting and heat treatment, time consuming chemical composition homogenization, cracking enhancement due to cooling contraction during solidification and quenching, tempering embrittlement, etc. [6].

One alternative approach for producing Fe-Mn-Si-Cr-Ni SMAs while avoiding most of CM drawbacks could be powder metallurgy (PM) which has been successfully applied to other SMAs, such as Ti-Ni, or to Cu base alloys [7].

Assuming that most of the difficulties in preparing grain refined microstructures of Fe-Mn-Si-Cr-Ni SMAs with homogenous structure can be eliminated by mechanical alloying (MA) [8], it is expected that one of its effects on PM Fe-Mn-Si-Cr-Ni SMAs would consist in increasing the solid-state solubility of alloying elements into Fe matrix [9].

Based on the above considerations as well as on the promising results reported by some of the present authors concerning stress induced formation of martensite in pre-strained [10] or mechanically cycled [11] hot rolled specimens obtained from a PM-MA Fe-18Mn-3Si-7Cr-4Ni SMA, the present paper aims to reveal MA-effects on the thermal behaviour of Fe-Mn-Si-Cr-Ni SMA powders subjected to heating up to 773 K.

2. Experimental details

Powder mixtures with nominal composition Fe-14Mn-6Si-9Cr-4Ni were prepared in tubular blender, from commercial powders. A part of the mixture was mechanically alloyed (MA'd) for 4h in SPEX™ D8000 high energy ball mill, using stainless steel vials and stainless steel milling balls under protective atmosphere. Comprehensive details concerning these operations were thoroughly given in a previous study [12].

In order to reveal MA-effects on powder mixtures subjected to thermal cycles, the powders were studied in two forms: (i) as blended, without MA, further designated as *0_MA* and (ii) as a mixture of equal amounts (50 %) of as blended and MA'd powders, designated as *50_MA*. Both powder mixtures were carefully sorted into several samples with initial masses of 40 mg.

Thermal cycles were applied by means of a NETZSCH STA 449 F3 device during a heating-cooling between room temperature (RT) and 773 K, under Ar atmosphere in previously mentioned conditions [13], at various rates from 0.4 to 10 K/min. Simultaneous thermal analysis (STA) comprises differential scanning calorimetry (DSC) and thermal gravimetry (TG)

measurements during temperature variation. The results were evaluated with PORTEUS software.

The structural changes occurring in powder mixtures as an effect of thermal cycling were analysed by means of a FEI Quanta SEM 200 3D dual beam microscope, with thermal chamber, able to develop both accelerated electron and focussed ion beam (FIB) fascicles and to heat up the specimens under protective atmosphere.

3. Experimental results and discussion

The DSC (heat flow variation) and DDSC (heat flow derivative variation) curves, recorded with a sample of *O*₂MA powder subjected to three consecutive heating-cooling cycles performed with 10 K/min, between RT and 773 K, are shown in Fig. 1.

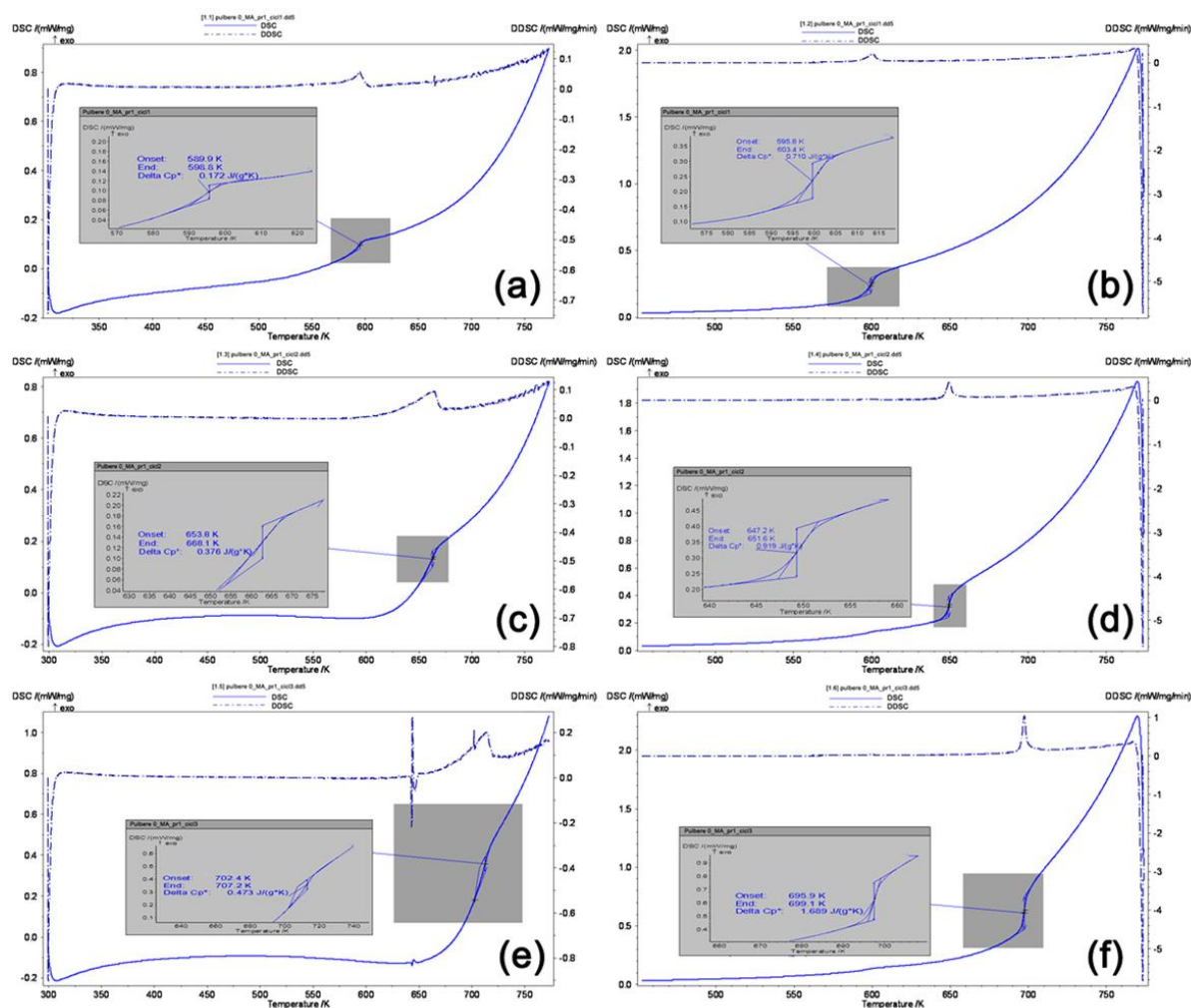


Fig. 1. Heat flow (DSC-solid lines) and heat flow derivative (DDSC-dash lines) variations with temperature, at a rate of 10 K/min, of *O*₂MA powders subjected to three consecutive thermal cycles: (a) 1st cycle heating; (b) 1st cycle cooling; (c) 2nd cycle heating; (d) 2nd cycle cooling; (e) 3rd cycle heating; (f) 3rd cycle cooling.

It is noticeable that an exothermic step occurred during each heating and an endothermic step accompanied each cooling stage. Considering the position of this reversible solid state transformation [14] as well as its typical aspect [15] it is assumed that these steps correspond to the ferromagnetic-paramagnetic (F-P) transition of Nickel, the Curie temperature of which lies in this thermal range. The grey enlarged insets show the evaluation of F-P transitions with PORTEUS software.

By qualitatively analysing Fig. 1 it seems that, with increasing the number of thermal cycles, the critical temperatures of the magnetic transition tend to move to larger values. This tendency is noticeable both on the

variation of DSC curves and on the variation of the DDSC curves, the local maxima of which tend to become more prominent with increasing the number of cycles. It is noticeable that the steps on the DSC curve, accompanying Ni magnetic transition are exothermic on heating and endothermic on cooling, in contrast to [15] where both steps have been exothermic.

The second set of calorimetric curves, corresponding to *50*₂MA powders subjected to the same experimental conditions as in Fig. 1, is shown in Fig. 2.

It seems that in *50*₂MA powders the magnetic transition has the same variation tendency during thermal cycling but occurs at higher temperatures.

In order to confirm the occurrence of the magnetic transition, temperature variation rate was decreased 25

times from 10 to 0.4 K/min, the results being shown in Fig. 3.

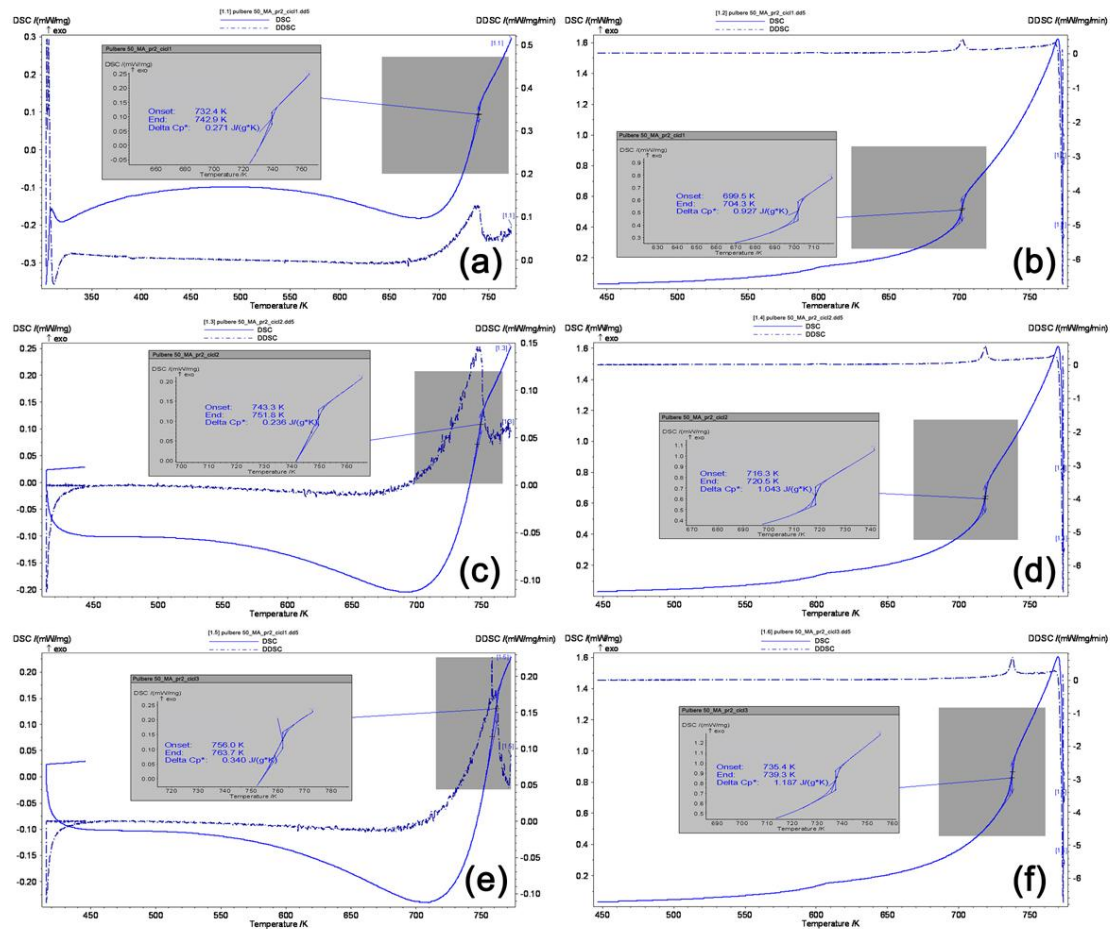


Fig. 2. DSC (solid lines) and DDSC (dash lines) variations with temperature, at a rate of 10 K/min, of 50_MA powders subjected to three consecutive thermal cycles: (a) 1st cycle heating; (b) 1st cycle cooling; (c) 2nd cycle heating; (d) 2nd cycle cooling; (e) 3rd cycle heating; (f) 3rd cycle cooling.

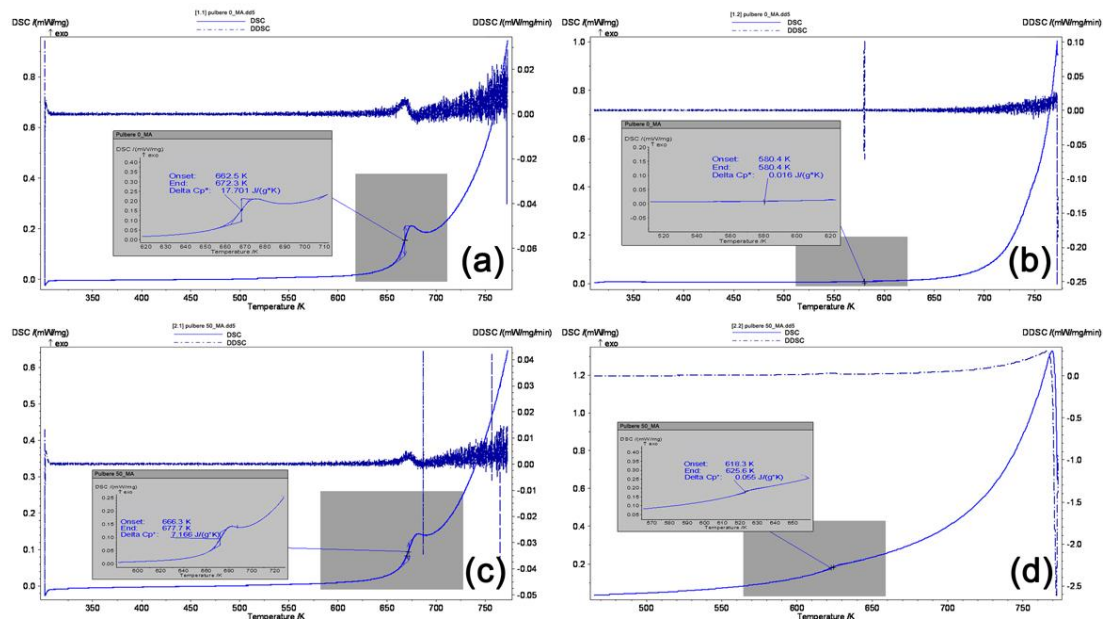


Fig. 3. DSC (solid lines) and DDSC (dash lines) variations with temperature, at a rate of 0.4 K/min: 0_MA powders during (a) heating and (b) cooling; 50_MA powders during (c) heating and (d) cooling.

The results obtained on heating with 0.4 K/min show a typical variation of heat flow corresponding to the F-P transition in pure Nickel [16].

As an effect of mechanical alloying and thermal cycling it is assumed that Ni atoms diffuse into neighbouring particles (such as Fe and Mn) and for this reason the steps shift more and more to larger temperatures [14] and become diffuse and eventually lost.

This disappearance is consistent with the fact that the anomaly, found in the temperature variation of the lattice spacing accompanying the F-P transition, is more pronounced in pure nickel than in nickel alloys [17]. This increase tendency of magnetic transition temperature in 50_MA powders could be regarded as a *first MA effect*.

A summary of the calorimetric data obtained from Figs. 1-3 is given in Table 1.

Table 1. Summary of the calorimetric data corresponding to Figs. 1-3.

	Temp. variation rate, K/min	Cycle no.	0_MA			50_MA		
			Onset, K	End, K	ΔC_p , J/Kg K	Onset, K	End, K	ΔC_p , J/Kg K
Heating	10	1	589.9	598.8	172	732.4	742.9	271
		2	653.8	668.1	376	743.3	751.8	236
		3	702.4	707.2	473	756.0	763.7	340
	0.4	1	662.5	672.3	17701	663.3	677.7	7166
Cooling	10	1	595.8	603.4	710	699.5	704.3	927
		2	647.2	651.6	919	716.3	720.5	1043
		3	695.9	699.1	1689	735.4	739.3	1187
	0.4	1	580.4	580.4	16	618.3	625.6	55

The *first MA effect* is obvious in regards of all critical temperatures of Ni magnetic transition, since in all cases the temperature values are larger at 50_MA than at 0_MA powders.

The *second MA effect* can be discussed in connection to increase tendency of critical temperatures listed in Table 1, during the cycles performed with 10 K/min. These temperature-increase values are listed in Table 2.

Table 2. Increase of the values of critical temperatures during the heating and cooling cycles applied with 10 K/min, K.

Process	Temperature increase from	0_MA		50_MA	
		Onset	End	Onset	End
Heating	1 st to 2 nd cycle	63.9	69.3	10.9	8.9
	2 nd to 3 rd cycle	48.6	39.1	12.7	11.9
Cooling	1 st to 2 nd cycle	51.4	48.2	16.8	16.2
	2 nd to 3 rd cycle	48.7	47.5	19.1	18.8

It is obvious that there are two opposite increasing tendencies of critical temperatures, between two consecutive cycles: 0_MA powders reveal lower augmentation from the 2nd to 3rd cycle than from the 1st to 2nd cycle while 50_MA powders always display larger increases from the 2nd to 3rd cycle than from the 1st to 2nd cycle.

A possible cause of this *second MA effect* could be related to the presence of a certain amount of amorphous phase in the MA'd fraction of 50_MA powders. Due to the severe constraints caused by MA processing technique [18], corroborated with particle refinement and lattice strain enhancement, an increase of the amorphisation degree [19] was noticed in MA'd quinary Fe-base alloys [20] even after milling times as low as 4 hours [21]. Moreover, our previous X-ray diffraction studies showed that Ni peaks decreased with increasing MA fraction and became more rounded [22]. It is further assumed that, during 1st heating, there is a larger quantity of Ni atoms diffusing into neighbouring particles in 0_MA powders

than in 50_MA powders, which contains a certain amount of amorphous state. Since more atoms diffuse, the increase of magnetic transition temperature will be larger. In 0_MA powders the largest amount of Ni atoms diffuses during 1st heating and there are less and less atoms able to migrate during 2nd and 3rd cycles. For this reason critical temperatures raised more from the 1st to 2nd cycle than from the 2nd to the 3rd. Conversely, during 1st heating a part of Ni atoms are trapped in the amorphous phase of MA'd powders and do not migrate. Assuming that a certain crystallization of the amorphous phase occurs on heating, as suggested by the endothermic flat minima preceding magnetic transitions in Figs. 2(a), (c) and (e), Ni atoms are released from amorphous regions. It follows that in 50_MA powders more Ni atoms are prone to migrate during 2nd and 3rd cycles causing larger increases in magnetic transition temperatures in these cycles.

Fig. 4 shows a set of SEM micrographs of 0_MA powders in initial state.

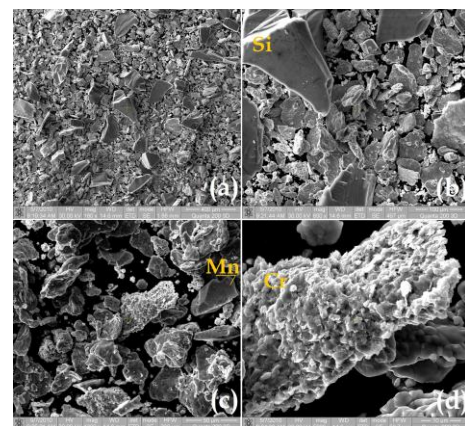


Fig. 4. SEM micrographs of 0_MA powders in initial state: (a) general aspect; (b) detail with larger Si particles; (c) general aspect of Cr powder with isolated Mn particles; (d) detail of Cr grain with sponge-like aspect.

The measured average sizes of the elemental particles range between 50–55 μm for Fe and 65–70 μm for Mn. The other particles are rather irregular. Thus, Si grains, Fig. 4(b), have an average size of 170 μm but their dimensions can be as large as 230 μm . Cr particles have sponge-like aspect as noticeable in Fig. 4(d) and dimensional range between 55–60 μm . Finally Ni particles are rather rare (since they occupy only 5 %) and generally small with dimensions less than 20 μm .

After a heating-cooling cycle, performed within the thermal chamber of the SEM-FIB device, only very slight changes of the structural aspect were apparent in the aspect of 0_MA powder sample, as depicted in the series of micrographs from Fig. 5.

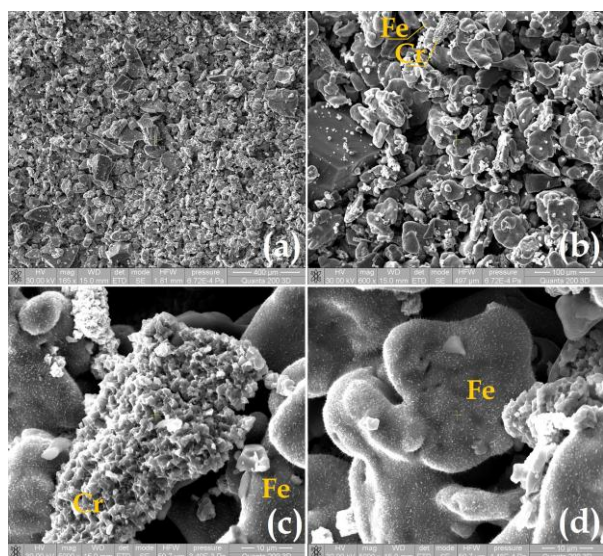


Fig. 5. SEM micrographs of 0_MA powders after 1st thermal cycle to 773 K: (a) general aspect; (b) magnified central zone of (a) with larger Fe and Cr particles identified in upper area; (c) detail of Cr particle; (d) detail of Fe particle.

Thus, the general aspect of the powder mixture remained almost the same if one compares Fig. 4(a) corresponding to initial state to Fig. 5(a). Fig. 5(b) shows a magnified image of the central zone from Fig. 5(a), where one particle of Cr and one of Fe were identified. These particles are detailed in Fig. 5(c) and (d), respectively. Cr particles have kept their sponge-like aspect and no particular levels of alloying contamination were measured by EDX on their surface. However, Fig. 5(d) reveals that the aspect of the surface of Fe particles has changed. Some white cilia-like outgrowths with micrometer-size lengths became visible on the surface of Fe particle. Since EDX analysis showed an increase of the oxygen amount up to approx 13 % on the Fe particle, it is assumed that these cilia-like outgrowths could belong to an iron oxide.

The next series of SEM micrographs correspond to 50_MA powder sample in initial state and is shown in Fig. 6. The average grain size range of the 50_MA powders, determined on Fig. 6(a) has been 45–50 μm . Average grain size decreased due to the contribution of the 50 % fraction

of MA powders. A detail of the central area of Fig. 6(a) is shown in Fig. 6(b) where two particles designated as MA and Cr are noticeable. Fig. 6(c) illustrates the formation in MA'd particle of cold weld bridges, as an effect of mechanical alloying processing.

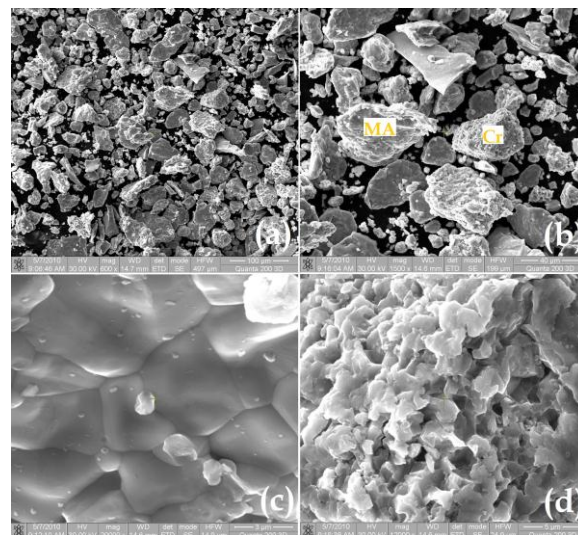


Fig. 6. SEM micrographs of 50_MA powders in initial state: (a) general aspect; (b) detail with two particles of MA and Cr; (c) enlarged view of MA'd particle revealing the presence of welded bridges; (d) enlarged view of Cr particle with sponge-like aspect.

On the other hand, the general aspect of the Cr particle which underwent no MA effect has been almost the same, in Fig. 6(d), as for 0_MA powders, in Fig. 4(d) or Fig. 5(c). This observation is valid for all elemental powder particles which were not subjected to MA processing.

Fig. 7 shows representative SEM micrographs of 50_MA powders subjected to a heating-cooling cycle.

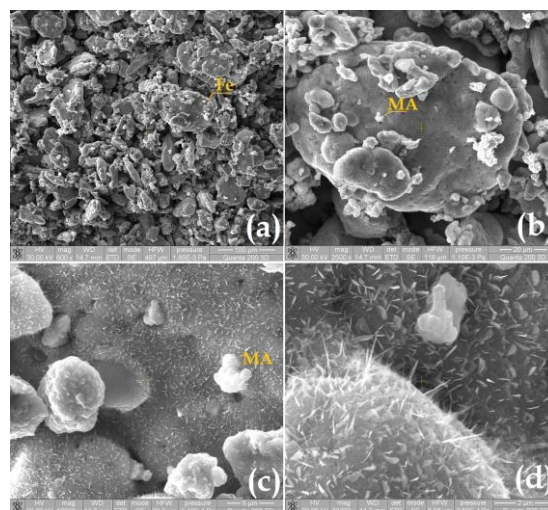


Fig. 7. SEM micrographs of 50_MA powders after 1st thermal cycle to 773 K: (a) general aspect; (b) detail of Fe particle; (c) magnified area with MA'd particle; (d) detail of cilia-like outgrowths.

In this case, as well, the general structural aspect of the powder mixture did not drastically change after a heating-cooling cycle, as noticeable in Fig. 7(a) as compared to Fig. 6(a) which illustrates the initial state. A larger Fe particle was selected as a landmark and the surrounding area was magnified in Fig. 7(b). Several smaller white MA'd particles, some of them partially incorporated into the large Fe particle, were identified by EDX. One of these white MA'd particles was chosen as reference and a detail of its surrounding Fe matrix was shown in Fig. 7(c). This MA'd particle has an average size of 3 μm .

Finally Fig. 7(d) shows the surface of the large Fe particle with one incorporated MA'd particle and various white cilia-like outgrowths the shape of the which are visible, as well, in 50_MA powders as they were in 0_MA powders. In this area, EDX analysis showed an increase of oxygen level up to approx. 20 %. So, it seems that the surface of Fe particles, which are present both in 0_MA and in 50_MA powder samples, became more oxidised when mixed with MA powders, since oxygen level reached approx. 13 % and 20 %, respectively.

A closer look of oxygen level variation on Fe particle surface was performed by EDX-FIB as shown in Fig. 8.

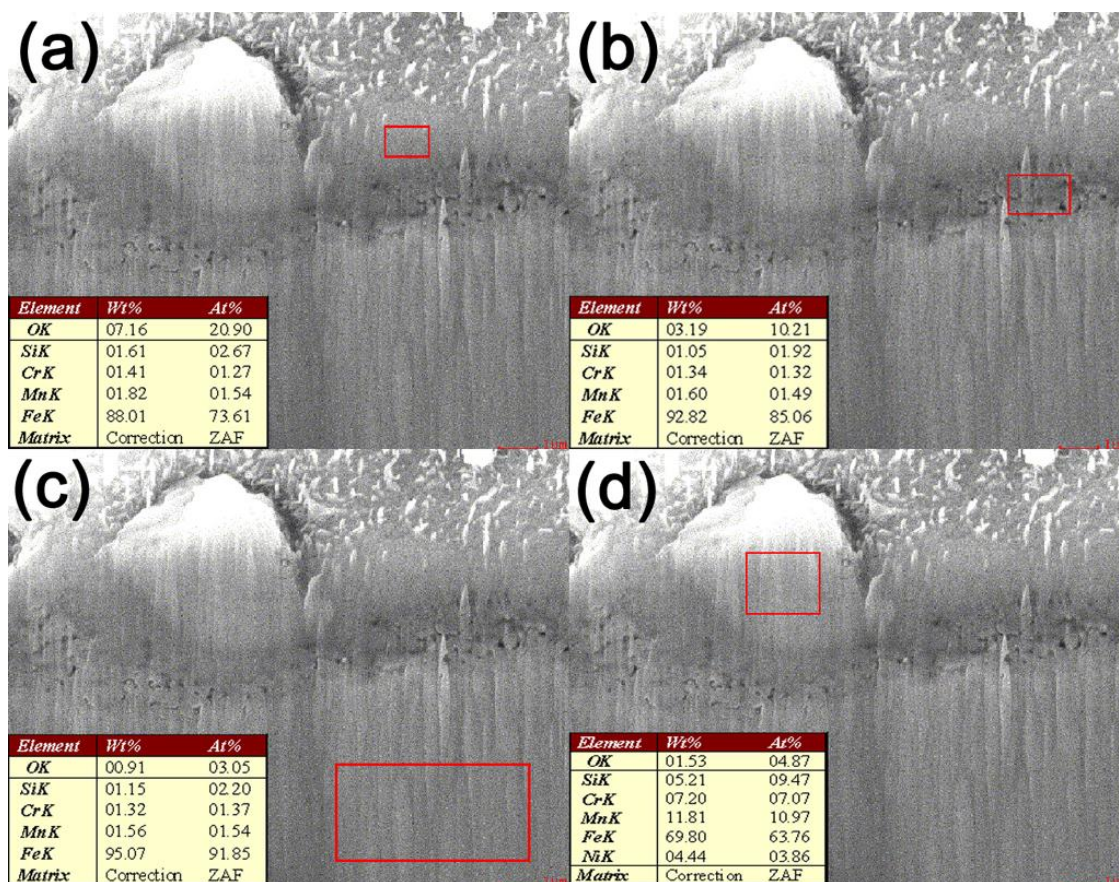


Fig. 8. Variation of chemical composition along FIB section into a Fe powder grain with incorporated MA'd particle, from 50_MA powder sample, subjected to a heating-cooling cycle to 773 K: (a) at the surface of the Fe powder grain; (b) below the surface of the Fe powder grain; (c) in the core of the Fe powder grain; (d) in the MA'd particle.

The chemical compositions determined at the surface in Fig. 8(a), below the surface in Fig. 8(b) and in the core of the Fe particle in Fig. 8(c), showed high Fe levels, very low Si, Cr and Mn amounts and decreasing oxygen levels, namely approx. 7%; 3% and 1 %, respectively. On the other hand, Fig. 8(d) demonstrates that the white particle could belong to the MA'd fraction of 50_MA powders and has an oxygen level of 1.5 %.

These variations suggest that, in spite of the protective atmosphere, there is a certain degree of oxidation which occurs much more intensely at the surface of Fe particles than at the surface of a part of MA'd particle which contain amorphous phase. These regions, with less

crystallinity, are present in the MA'd fraction of 50_MA powders and partially crystallize during 1st heating, thus releasing Ni atoms that undergo magnetic transition during 2nd heating cycle. Surface oxidation occurs more intensely in commercial as blended powders than in the amorphous regions, which are admitted to exist in the MA'd fraction of 50_MA powders, since amorphous structures are more resistant to corrosion than crystalline ones.

In order to prove that oxidation really occurred during the heating-cooling cycles, in spite of the protective atmospheres employed both at STA (argon) and in SEM (nitrogen), mass increases, observed by TG, are exemplified in Table 3, and Fig. 9 for 0_MA powders.

Table 3. Mass increase during heating at 0_{MA} powder, %.

	Maximum heating temperature, K		
	773	873	973
1 st cycle	0.39	2.58	0.27
2 nd cycle	0.27	0.3	0.52

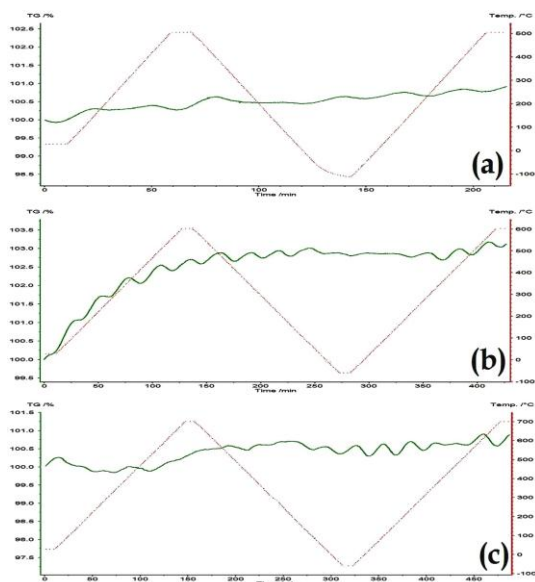


Fig. 9. TG thermograms of three 0_{MA} powder samples subjected to heating-cooling-heating thermal cycling, with 10 K/min, between RT and: (a) 773 K; (b) 873 K; (c) 973 K.

During the three series of heating-cooling-heating cycles slight mass fluctuations are noticeable but there is a general mass-increase tendency which was also shown in Table 3. Both the mass increase and the augmentation of oxygen amount from the core to the surface of particles suggest the occurrence of an oxidation phenomenon, which seems to be more intense at the level of elemental particles (specially at Fe) than at the level of MA'd particles.

4. Conclusions

In powder mixtures of as blended and mechanically alloyed particles with nominal composition Fe-14Mn-6Si-9Cr-5Ni (mass. %) three phenomena were observed during thermal cycling: (i) magnetic transition of Ni; (ii) glass-transition of amorphous regions present in MA'd powders and (iii) surface oxidation.

The *first MA effect* consisted in the increase of magnetic transition temperatures due to the formation of solid solutions as an effect of Ni atoms migration from pure Ni powder into pure Fe and Mn powder particles.

The *second MA effect* was generated by the presence of a small fraction of amorphous phase which partially crystallized during each heating, thus releasing Ni atoms which dissolved into surrounding regions and increased the amount of solid solution.

Surface oxidation occurred mostly in as blended pure Fe particles.

Acknowledgments

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