PROCESSING OF DENSE Fe–BASED ALLOYS WITH FINE MICROSTRUCTURE VIA SHORT DISTANCE INFILTRATION OF LOW MELTING PHASE

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Abstract

Dense Fe-Co and Fe-Co-Ni based alloys and composites with an addition of hard particles were fabricated employing the developed Short Distance Infiltration (SDI) processing route. During SDI processing, a non-dense compact containing 5 to 20 % of low melting phase is heated rapidly up to temperature above the melting temperature of the low melting phase. Then pressure is applied resulting in extrusion of the formed liquid into pores and leading to full densification. Ag-Cu and Cu-Mn-Sn prealloyed powders were used as low melting temperature phases. Processing temperatures were in the range of 750-900°C and pressures applied were in the range of 50-200 MPa. WC carbide particles were added as a hard wear resistant phase. The use of fine micron size Fe, Co and Ni powders in SDI processing resulted in fine microstructure. Microstructure was characterized employing XRD and SEM/EDS. High transverse rupture strength accompanied by high microhardness was obtained for a number of compositions and processing conditions. SDI processing route can be used also for the processing of other alloys and metal-ceramic composites containing a large volume fraction of hard particles.

Keywords: Fe-based alloys, short distance infiltration, full density consolidation, fine microstructure, mechanical properties

INTRODUCTION

Full density and fine microstructure are the main requirements for high performance structural materials. There are a number of approaches for processing of metal matrix composite (MMC's) materials by powder metallurgy methods, such as: hot pressing or HIP of powder blends or powder/fibre blends, infiltration, squeeze casting, liquid phase sintering, reactive synthesis of in situ composites, including reactive infiltration, flame and plasma spraying of agglomerated metal-ceramic particles, and more [1]. Hot pressing or HIP to full density of MMC's and especially those containing a large volume fraction of hard particles, requires relatively high pressures and long exposures making the processing expensive [2]. During reactive synthesis of in situ composites, pressure should be applied to compensate the intrinsic negative volume change and often a combination of relatively high temperature, pressure and long exposures are required to obtain dense materials [3,4]. Processing via liquid state enhances consolidation to full density. Liquid phase sintering is widely used for fabrication of cemented carbides and heavy alloys [5,6] – still the

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processing is quite slow and a coarsening of microstructure takes place. In infiltration technique, a capillarity effect is used – low melting temperature liquid is infiltrated into solid skeleton [7]. Wetting of the skeleton by liquid is important, and the finer the interconnected pore system, the finer the structure of the composite. Processing of employing liquid phase sintering and infiltration results in residual tensile stresses in the low melting phase. In squeeze casting and reactive infiltration the liquid phase is impregnated into the solid skeleton under the pressure – the finer the pores, the higher should be the pressure applied to obtain a dense product [8,9]. During reactive infiltration, as a result of reaction, the pores are closed and it is difficult to squeeze the liquid through the fine pores and long distances and thus to obtain a fine microstructure in bulk structural parts. Preparation of dense compacts made from blends containing very fine particles of low melting phase, followed by a rapid heating to temperature above melting of this phase may result in a dense composite, especially when the solid matrix is dissolved in the melt – such a processing route was described in [10] as Super-Transient Liquid Phase Sintering. Recently, a novel rapid processing route of composites was developed – pressure assisted Short Distance Reactive Infiltration (SDRI): during fast heating of 70-80 %, dense compacts containing a low melting phase above the melting temperature, T_m, of such a low melting phase followed by the application of pressure, the liquid formed is extruded from larger size "lakes" into pores, resulting in rapid consolidation to full density followed by a reaction with the solid phase and formation of *in situ* composites [11,12]. SDRI is one of the routes of the Thermal Explosion Mode of SHS (Self-Propagating High-Temperature Synthesis). SDRI was used for fabrication of dense *in situ* intermetallic and ceramic matrix composites. In the present work, the approach of SDRI is expanded also to SDI – Short Distance Infiltration without a pronounced reaction between the liquid phase and the solid matrix – for the processing of dense MMC's with fine microstructure.

EXPERIMENTAL

Fine powders of Co (1-2 μm) from Eurotungsten, carbonyl Fe (1-3 μm) from BASF, Ni (1μm) from CERAC were used for preparation on Fe-Co and Fe-Co-Ni matrix blends. Low melting phase powders: Ag-28Cu eutectics (-325 mesh) from "Silmet" (Israel), Al(-325 mesh) from CERAC and Cu-23Mn-17Sn (-325 mesh) - special order from CERAC were used in the experiments. The melting point of Ag-Cu eutectic $T_m = 780°C$, for Al $T_m = 660°C$ and for Cu-23Mn-17Sn alloy $T_m = 770°C$. WC (1-2 μm) from Starck was used as hard particles. Powder blends 50Fe-50Co and 70Fe-20Co-10Ni were prepared by 2h high energy attrition milling with 2.5 grinding media-to-powder ratio. (All compositions and blends are in mass %). 10 % of Ag-Cu eutectic was admixed to the 50Fe-50Co attrition milled blend and milled for an additional 15 min with the resulting composition: 45Fe-45Co-10Ag. 10 % of Cu-23Mn-17Sn was admixed to the 70Fe-20Co-10Ni blend and milled for an additional 15 min with the resulting composition 63Fe-18Co-9Ni-10(Cu-23Mn-17Sn) or 90(70Fe-20Co-10Ni)-10(Cu-23Mn-17Sn). 5 % of Al was admixed to 50Fe-50Co blend and milled for an additional 15 min with the resulting composition 45Fe-45Co-10Al. Fine WC particles were added to the main compositions on the first stage of attrition milling.

18 mm diameter 15 g compacts were prepared from the blends at pressures 400-500 MPa, resulting in about 75-80 % of theoretical density. The compacts were annealed in hydrogen flow (500°C) in order to remove oxide layers from the metal powder surfaces. After reduction treatment, compacts were placed into preheated die which was placed between preheated rams on an Instron testing machine under a relatively low pressure of 5÷10 MPa to ensure rapid heating of the compact (the compact was heated from the walls

of the die) but avoiding plastic deformation of the matrix. The die, 18 mm inner diameter and 30 mm outer diameter, was heated in the furnace to the same temperature as the rams. The temperature of the die and of the rams was, as a rule, above the T_m, of the low melting phase. The temperature of the compact in the preheated die was measured by thermocouple – usually the specimen was heated to the temperature of the die in 30 s or less. The rapid heating was especially important for compositions with al as a liquid phase, since solid state reactions of Al with Fe and Co with the formation of Fe and Co aluminides can take place. When the temperature of the compact was approaching the temperature of the die, a higher pressure of 50-200 MPa (depending on overheating above the T_m,) was applied. This resulted in a squeezing of the molten phase into the pores and is referred to as Short Distance Infiltration (SDI), and compared to the SDRI (Short distance Reactive Infiltration) described in [11,12], proceeds without a pronounced reaction. The schematic of SDI is shown in Fig.1. Compared to the traditional melt infiltration, SDI has the advantage of considerably shorter infiltration distances (microns vs. millimeters/centimeters). SDI promotes consolidation to full density at it may not, or may be, followed by a reaction with the solid matrix. Reaction of the liquid with the matrix may result in a new product or partial conversion as is shown in Fig.1. The specimens were cooled below T_m under pressure to avoid residual tensile stresses in the low melting phase after solidification.
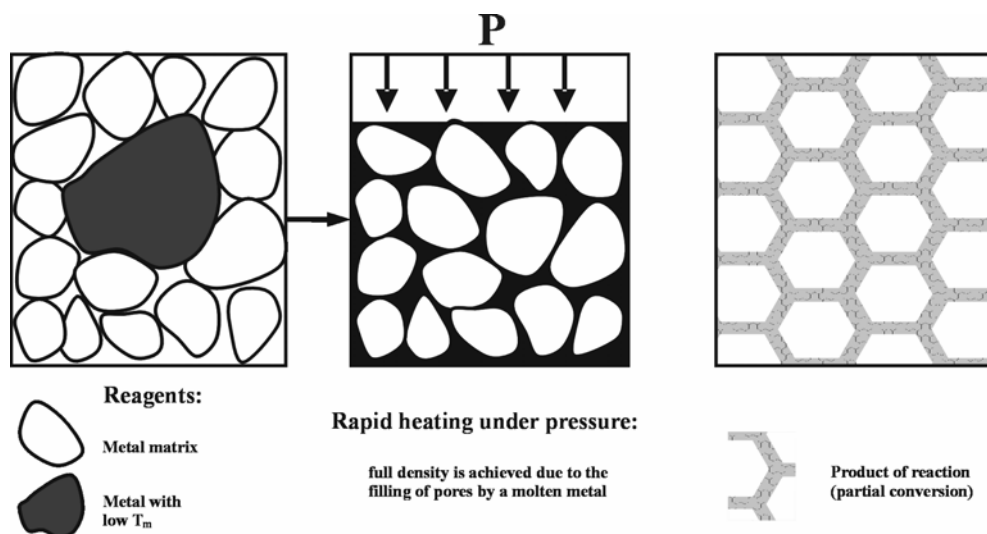

Fig.1. Schematic of Short Distance Infiltration (SDI).

After processing, the microstructure and phase composition were characterized by X-ray diffraction (XRD) and electron scanning microscopy (SEM) with chemical analysis (EDS). Samples of 18x4x4 mm^3 were cut from the specimens, prepared via SDI or SDRI and polished. Three point bending tests (transverse rupture strength, σ_{TRS}) were performed employing the Instron testing machine with a cross head speed of 0.1 mm/min. Microhardness of consolidated specimens was measured at a 200 g load.

RESULTS AND DISCUSSION

Matrices with Ag-Cu eutectic as low melting phase

72Ag-28Cu eutectic has a relatively low melting temperature, $T_m = 780°C$. Ag is not dissolved in Co and Fe, and Cu is only slightly dissolved in solid Co or Fe. Thus matrices based on Co, Fe or their alloys are a good model for processing *via* the SDI route. A number of compositions based on Co, Fe and their alloys were investigated. As it was mentioned earlier, in the SDI route non-dense compacts are rapidly heated above melting temperature of the low melting phase under relatively low pressure, 2-5 MPa (the pressure on this stage is applied only to assure rapid heating from the pressure cell walls), and then higher pressure is applied (P = 40-200 MPa, depending on composition and processing temperature) resulting in extrusion of the liquid phase into the pores. For comparison, experiments were performed when a higher pressure was applied at T below T_m. As it can be seen from SEM micrographs in Fig.2 for composition 45Co-45Fe-10Ag/Cu eutectic hot pressed at T = 760°C below T_m, relatively large regions of low melting phase are retained (Fig.2a), corresponding to the initial size of Ag-Cu powder, while for specimens processed at temperatures above T_m, very fine regions of Ag-Cu phase are observed (Figs.2b and 2c) with a very homogeneous distribution of this phase. In specimens prepared at 780°C melting temperature, both relatively coarse as well as fine regions of Ag-Cu eutectic are observed (Fig.2d).
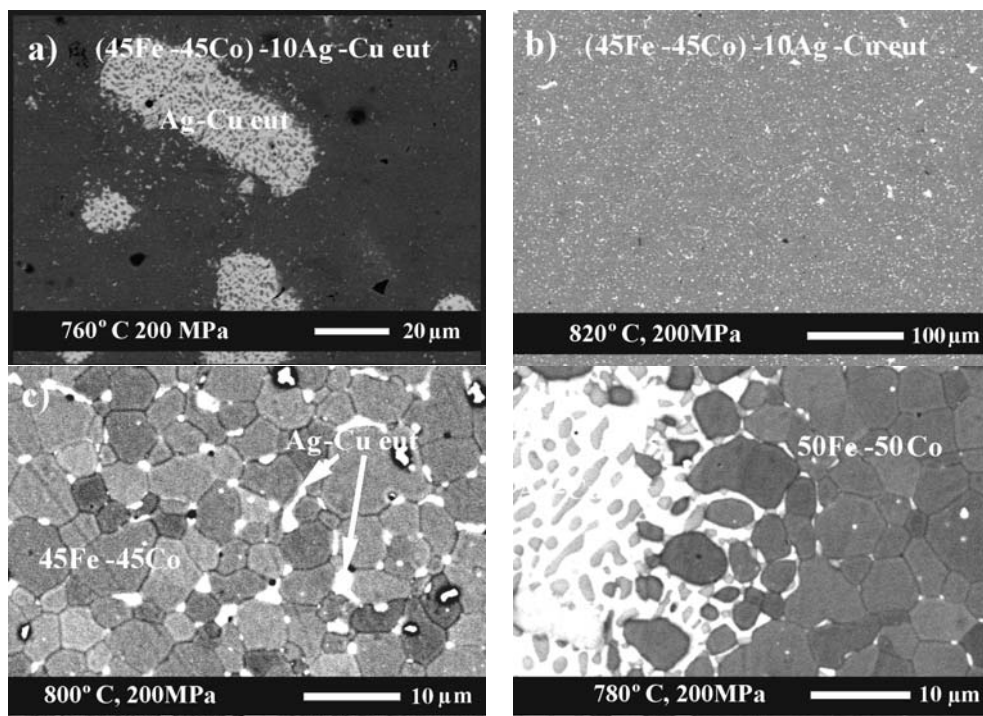

Fig.2. SEM micrographs of polished specimens prepared via hot pressing
of 45Co-45Fe-10Ag/Cu eutectic: a) at 760°C, b) at 820°C, c) at 820°C, and d) at 780°C.

Mechanical properties of 45Co-45Fe-10Ag/Cu specimens processed *via* SDI are also higher: VHN = 320±10 kg/mm^2 and σ_{TRS} = 1250±60 MPa as compared to 280±15 kg/mm^2 and 1020±70 MPa, respectively, for the corresponding specimens hot pressed at 760°C. Similar results were obtained for a Co matrix with 10 wt.% Ag-Cu eutectic, as well as for compositions with as low as 5 wt.% Ag-Cu eutectic. This aspect is important since Ag-Cu eutectic containing 72 % Ag is expensive.

Matrices with Cu-23Mn-17Sn as low melting phase

The alloy Cu-23Mn-17Sn was fabricated by rapid solidification on a special order. The melting temperature of the alloy is about 770°C, slightly higher than that of Ag-Cu eutectic but the price is about 25 % of the price of Ag-Cu eutectic. In addition, Mn forms unlimited solid solutions with Co and Fe, and Sn may form intermetallics with Co and Fe, as well as with Cu and Mn. A number of compositions were prepared, based on Co, Fe as well as Co-Fe and Fe-Co-Ni alloys without and with the addition of hard particles. In all cases, when the higher pressure was applied at temperatures above 800°C - T_m of this Cu-23Mn-17Sn alloy, dense specimens with very fine homogeneous structures were obtained. Very good mechanical properties, with an excellent bonding integrity of coated diamonds to the metal matrix were obtained for the Fe-20Co-10Ni-10Cu/Mn/Sn alloy. Examples of microstructures of such composition after various processing temperatures are shown in SEM micrographs in Fig.3 (fracture surfaces). It can be seen that the microstructure remains very fine even after processing at 1000°C. The same applies to similar compositions with the addition of 10 wt.% WC (Fig.4). EDS analysis shows that Mn is mostly dissolved in a FeCoNi alloy, while very fine Cu and Sn rich regions are homogeneously distributed in the matrix.
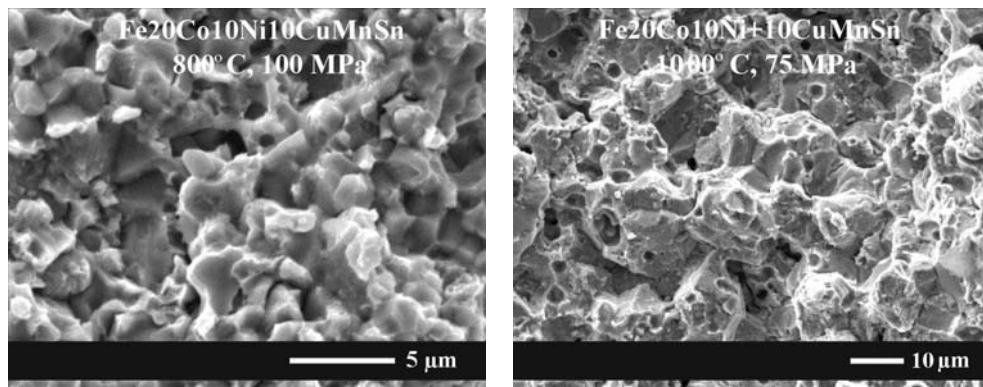

Fig.3. SEM micrographs (fracture surfaces) of specimens processed via SDI for Fe-20Co-10Ni alloy with Cu-23Mn-13Snas a liquid phase with a low melting temperature (T_m = 770°C).

The processing parameters and mechanical properties obtained for materials based on composition Fe-20Co-10Ni-10Cu/Mn/Sn, both without and with the addition of WC particles are presented, respectively, in Tables 1 and 2. It can be seen that high microhardness, VHN and σ_{TRS} are obtained for various processing conditions even at short processing cycles, t(T) – exposure under pressure at temperature for 5 min. For specimens without WC, an increase in temperature results in an increase of VHN and decrease in σ_{TRS}, and at longer exposures, some decrease of VHN and a decrease of σ_{TRS} is observed, most probably as a result of homogenization and partial coarsening of the microstructure. Higher

VHN but lower σ_{TRS} were obtained for specimens with additions of WC. Preliminary experiments show that an addition of WC results in a pronounced increase of wear resistance against SiC grinding wheal.
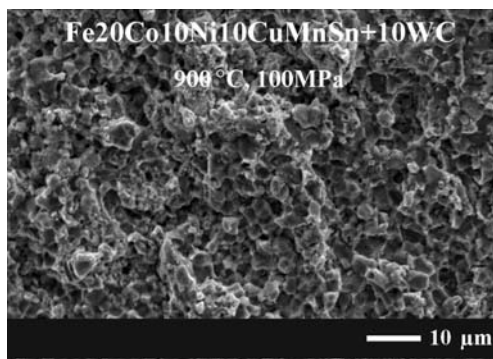

Fig.4. SEM fracture surface of a specimen processed at 900°C via SDI from Fe-20Co-10Ni +10WC alloy with Cu-23Mn-13Sn as a liquid phase with low T_m.

Tab.1. Processing conditions and obtained properties for composition Fe-20Co-10Ni + 10(Cu23Mn17Sn).

Number	Temperature T [ºC]	Pressure P [MPa]	Exposure t(T) [min]	Microhardness VHN [kg/mm^2]	Transverse rupture strength, σ_{TRS} [MPa]
1	800	100	5	390	1910
2	800	100	25	380	1560
3	825	100	5	400	1590
4	825	100	25	390	1350
5	850	100	5	425	1590
6	850	100	25	405	1280
7	900	75	5	415	1430
8	900	75	25	360	1350

Tab.2. .Processing conditions and obtained properties for composition Fe-20Co-10Ni + 10(Cu23Mn17Sn) + WC.

Number	% WC	Temperature T [°C]	Pressure P [Mpa]	Exposure t(T) [min]	Microhardness VHN [kg/mm^2]	Transverse rupture strength σ_{TRS} [MPa]
1	5	900	100	5	405	1360
2	10	800	100	5	370	1200
3	10	850	100	5	410	1100
4	10	900	100	5	460	1240
5	15	900	100	5	410	1340

Fe-Co matrix with Al as a low melting phase

Composition based on composition: 45Fe-50Co matrix with 10 wt.% Al (about 14 vol.%) as low melting phase were also processed employing SDI with rams at temperatures of 800°C. Extrusion of liquid al into the pores results in densification and is followed by a reaction of Al with Fe and Co, with the formation of Fe and Co aluminides and total consumption of Al. Self-heating to about 920°C as a result of exothermic reactions was observed as it takes place during SDRI [11,12]. Such additional heating being a result of exothermic reactions may promote densification to full density and can be used also in other systems.

The microhardness for the 45Fe-45Co-10Al composition processed *via* SDRI is high: VHN = 450±20 kg/mm^2 as compared to 320±10 kg/mm^2 for 45Fe-45Co-10Ag/Cu eut., but the specimens are more brittle with σ_{TRS} = 1040±50 MPa as compared to σ_{TRS} = 1250±60 MPa for 45Fe-45Co-10Ag/Cu eut., processed via SDI at 760°C.

Preliminary results show that for compositions 75 at. % Fe - 25 at. % Al and 50 at. % Fe - 50 at. % Al SDRI at 800°C and above, results in dense products with structure according to XRD patterns of intermetallics Fe$_3$Al and FeAl correspondingly.

CONCLUSIONS
- Dense Fe-Co and Fe-Co-Ni based alloys and composites with an addition of hard particles were fabricated employing the developed Short Distance Infiltration (SDI) processing route with Ag-Cu eutectic and Cu-Mn-Sn alloy as low melting phases.
- Very fine microstructures and high mechanical properties were obtained for the specimens fabricated via SDI route.
- SDI processing route with Cu-Mn-Sn as low melting phase was employed successfully also for the fabrication of composite containing 70 vol. % of hard WC particles, and can be used for processing of other MMC's.

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