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COBALT ALUMINIDE SYNTHESIS BY SHS REACTION AND ITS APPLICATION AS REINFORCEMENT OF COPPER MATRIX COMPOSITES

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The porous single-phase CoAl compound powder synthesized by self-propagating high-temperature synthesis (SHS) was used as the reinforcement phase to produce the dense CoAl/Cu (50 wt.%Cu) metal matrix composite by solid-state (SSS) and liquid-phase sintering (LPS), at 750 and 1150°C, respectively. Multiscale microstructure characterization was carried out in terms of X-ray diffraction, scanning and transmission electron microscopy in order to reveal reaction and sintering mechanisms. The results indicate that the LSP conducts to higher relative density of around 98.5% compared with the SSSed case of 95%. During the LSP process, the effective diffusion of molten Cu, promoted by capillary aspiration of the liquid, allows to fully fill the pre-existing pores of the SHSed CoAl to form sub-micrometre sized Cu precipitates homogenously dispersed within the reinforcement particles. The formation of sub-micrometre sized rod-like CoAl precipitates in the Cu matrix is caused by the solution-precipitation mechanism. The microhardness measured in the CoAl reinforcement particles and Cu matrix of the LPSed composite, being higher than those of the SSSed one, is discussed to be associated with the resultant microstructure.

Keywords: matrix composite; intermetallic compound; SHS; liquid-phase sintering; microstructure.

1. Introduction

Aluminides of the transition metal have attracted a lot of interest in research over the last decades, in particular for structural applications at high temperature due to their combination of good mechanical properties, relatively low density and high melting point [1-4].

The presence of aluminium further contributes to good resistance to oxidation as well as corrosion even in aggressive environments. Indeed, an

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adherent passivation layer of alumina (Al_2O_3) in a few nanometres in thickness forms on the surface providing effective protection [5-7].Many efforts have been devoted to the formation of aluminides having relatively high melting temperatures, such as NiAl [8-9], FeAl [10-12] and TiAl [13-14], by combustion-like exothermic reactions using self-propagating high-temperature synthesis (SHS). However, these SHSed intermetallic compounds are often porous and have a spongy structure due mainly to the violent nature of synthesis reaction [15]. In order to develop the dense material, researchers have combined complementary techniques, such as mechanically activated SHS (MASHS) [16] and mechanically activated field-activated pressure assisted synthesis (MAFAPAS) [17].

Among the well-known aluminides, CoAl intermetallic compound is also a promising material for many high-temperature applications due to its high melting temperature of around 1648°C, moderate oxidation resistance and thermal conductivity [18]. As a result, it has various applications such as heterogeneous catalysts [19], metallization layers of III-V semiconductor devices [20]. However, only a few relevant studies have been carried out to the synthesis and characterization of CoAl [21-23] and to the evaluation of its mechanical properties [24], perhaps because of its limited application potential until recently. The main obstacle for using such an intermetallic as the structural material is its low ductility and toughness at room temperature [25].

Reinforcing CoAl with hard ceramics to the formation of intermetallic matrix composites (IMC) is one of the effective solutions. It has been reported that homogenous dispersion of the second-phase hard particles (e.g. Al_2O_3) in the intermetallic matrix can improve the mechanical properties [26]. In contrast, the particular interest has been attributed to integrate CoAl as the reinforcement phase into metal or ceramic matrices (i.e. the formation of ceramic (CMC) or metal matrix composites (MMC)) [27-28]. Regarding the MMC, the choice of Cu as the matrix material is motivated by its good complementarity of properties with respect to CoAl. Indeed, it is expected that the combination of excellent hardness and resistance to oxidation of the CoAl reinforcement and good ductility of the Cu matrix can provide the formed CoAl/Cu MMC with good impact strength, mechanical strength and, in return, possible use of such a composite under severe service conditions. Hence, the objectives of this work aim at (i) processing of the CoAl/Cu MMC by synthesis of the CoAl compound using SHS reaction followed by sintering at the solid and liquid states and (ii) evaluation of relative density and microhardness and microstructure characterization, in terms of X-ray diffraction (XRD), scanning (SEM) and transmission electron microscopy (TEM), in order to reveal reaction and sintering mechanisms.

2. Experimental procedure

2.1 Starting materials and processing

The raw materials used in this work were the commercial cobalt, copper and aluminium powders provided by the firm Good Fellow. Their main characteristics are given in Table 1.

Table 1

Characteristics of the starting powders

Powder	Purity (%)	Particle diameter (μm)	Specific area (cm^2/ml)
Cobalt (Co)	99.5	10.19	16.159
Copper (Cu)	99.9	bimodal:13.6 and 120	1.579
Aluminium (Al)	99.5	55.52	1.492

In order to synthesize the CoAl compound, the Co-50 at.% Al (i.e. Co-31.4 wt.% Al) powder mixture was prepared and homogenized in a mechanical mixer for 30 minutes. Disc samples of 4 mm in height and 13 mm in diameter were compressed at room temperature by applying uniaxial compression of 300 MPa in a stainless-steel pelletizer. SHS reaction was carried out in a sealed enclosure under an argon protective atmosphere, which was initiated by a tungsten heating resistor placed about 1 mm away from the sample. The SHSed CoAl product was manually grounded in an agathous crucible. Then, the homogenous CoAl (50 wt.%)/Cu powder mixture was prepared, compressed under uniaxial pressure of 300 MPa at room temperature and sintered at 750 and 1120°C (i.e. solid-state (SSS) and liquid-phase sintering (LPS), respectively) in order to acquire the composite with full density. Note that the melting temperature of pure Cu is around 1083°C. The heat treatment was carried out under a dynamic argon flow for one hour hold time, followed by natural cooling. Relative density was measured by the Archimedes method and 5 measurements were used to obtain an average value given in this paper.

2.2 Microstructure characterization and microhardness measurement

XRD examination was done using a BRUKER D8 diffractometer with Cu-K_α radiation ($\lambda = 1.5418$ Å). 2θ scans were performed from 20 to 120° with a scan speed of 1,2°/min. CoAl (JCPDS 44-1115) and Cu phases (JCPDS 04-0836) were used for indexing diffracted peaks. Cross sections of the SHSed CoAl and CoAl (50 wt.%)/Cu composite samples were mechanically polished and examined using a Philips XL30 environmental and a JEOL JSM-7800F SEM instruments, both operated at 15 kV. The latter was equipped with a field emission gun (FEG) and an Oxford energy dispersive X-ray (EDX) spectrometry system. The composite TEM sample was prepared by mechanical thinning followed by ion milling using a Gatan Model 691 precision ion polishing system to electron transparency. A Philips CM30 transmission electron microscope, operated at 300 kV and equipped with a Bruker EDX spectrometry system, was used for TEM examination. Microhardness (HV 0.05) tests of the mechanically polished composite samples were carried out and 10 measurements of reinforcement and matrix regions each were used to obtain an average.

3. Results and discussion

As shown by XRD in Fig. 1a, the present SHS condition conducts to the formation of the stoichiometric CoAl compound by almost totally consuming the starting elemental Co and Al powder mixture. The SEM image of the synthesized powder sample (Fig. 2a) reveals the uniform grey contrast corresponding to the single-phase CoAl compound, being in agreement with the XRD result, and a large amount of large porosity. It has been reported that the combustion reaction between Co and Al particles is highly exothermic such that the synthesis of CoAl is self-sustained upon initiation even without any preheating prior to ignition and the activation energy of around 121.7 kJ/mol is estimated [22]. The SHS mechanism of the CoAl powder compact is attributed to the melting of Al followed by the dissolution of solid Co into the molten liquid to yield the CoAl. This is because the measured combustion temperature as high as the melting point of Co (around 1495°C) is not reached being independent on the SHS parameters like the particle size [23]. However, the use of coarse Al and fine Co particles in this work may result in high porosity in the final product due to volume expansion during the SHS process.

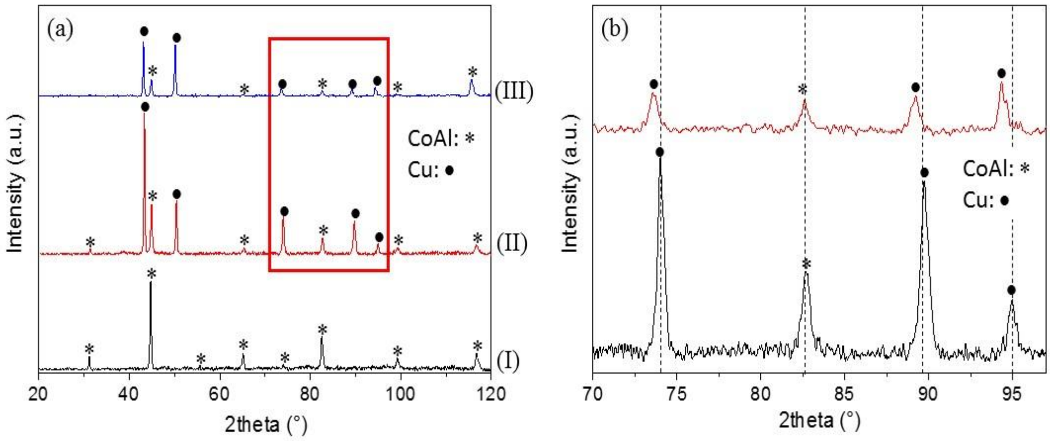

Fig. 1. (a) XRD patterns of the SHSed CoAl compound (I), the SSSed (II) and LPSed CoAl (50 wt.%)/Cu composites (III) and (b) the zoom-in XRD patterns of the rectangle box in (a) highlighting the shift of Cu peaks in the LPSed composite in comparison with the SSS case.

The XRD results of both sintered composite samples (Fig. 1a) show the presence of CoAl and Cu phases and no other additional phases are detected. Further, it is clear in Fig. 1b that the Cu peaks of the LPSed composite are systematically shifted towards the low angle range indicating an increase in the lattice parameter of Cu. XRD peak shift is generally related to the different types of internal stresses and planar faults, especially stacking faults or twin boundaries [29]. In this case, the swelling of the Cu mesh most possibly originates from the substitution of Cu atoms by Co and Al atoms in the Cu lattice due to their high solubility in Cu at high temperature and incomplete precipitation process relating to rapid cooling. The SEM image of the SSSed composite (Fig. 2b) displays the micrometre-sized irregular-shaped CoAl reinforcement particles embedded in the Cu matrix. Certain small porosity, witnessed by the measured relative density of around 95%, also presents in the matrix and, in particular, within the CoAl particles. Comparatively, the SEM result (Fig. 3) of the LPSed composite shows Cu-rich sub-micrometre sized precipitates homogenously dispersed within the CoAl reinforcement particles. This suggests that molten Cu is diffused into the pre-existing sub-micrometre sized pores of the SHSed CoAl particles. This sample has the relative density of around 98.5% which is higher than the one processed by SSS. Only a few small porosities at the interfacial area are visible, while it is almost fully dense within the CoAl reinforcement. The spherical feature of the CoAl particles and the sub-micrometre sized elongated precipitates rich in Co and Al in the Cu matrix also suggest that the dissolution-precipitation mechanism is occurred at the edges of the CoAl particles. Furthermore, the combination of electron diffraction and TEM/EDX mapping allows to identify the nature of both above-mentioned sub-micrometre sized precipitates visible in the CoAl reinforcements and Cu matrix.

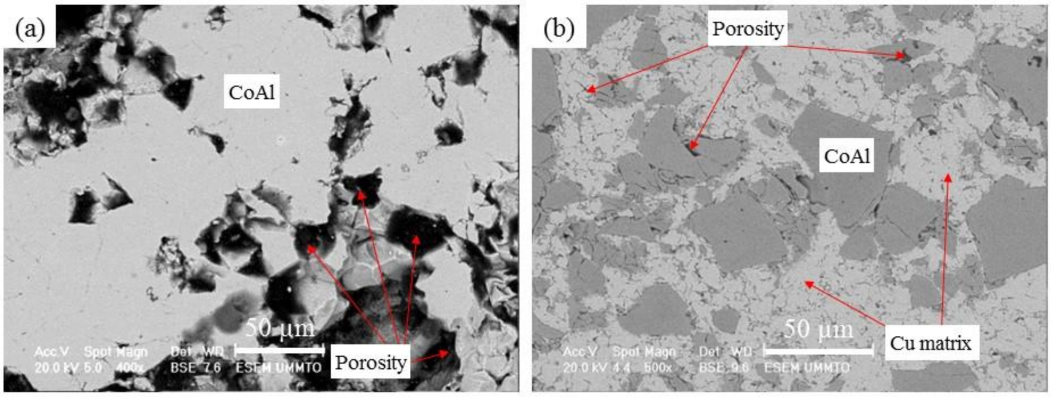

Fig. 2. Backscatter-electron (BSE) SEM images showing (a) the SHSed CoAl compound and (b) the SSSed CoAl (50 wt.%)/Cu composite

Being in agreement with the XRD results, it is found that the precipitates in the CoAl particles and Cu matrix correspond to the Cu and CoAl phases, respectively.

In the typical situation of LPS, there are dissolution processes at the compound/liquid matrix interface, which also causes particle rounding. This partial solubility causes the liquid to wet the solid, providing a capillary force that pulls the particles together for rapid densification. At the same time, the high temperature softens the solid, further assisting densification. High-diffusion rates associated with the liquid give rise to fast sintering. Liquid phase also enhances the reinforcement/matrix bonding which is beneficial for overall mechanical properties of the composite [30]. The pre-existing porosity of the CoAl reinforcement particles, due to its small sub-micrometre size, is easily filled to form the Cu dispersed precipitates accentuated by capillary aspiration of the liquid. This significantly increases the HV of the

Table 2

Microhardness measured in the CoAl reinforcement and Cu matrix of the composites processed by SSS and LPS

Sintering temperature (°C)	CoAl reinforcement (HV 0.05)	Cu matrix (HV 0.05)
750 (SSS)	182±34	101±13
1150 (LPS)	313±25	132±9

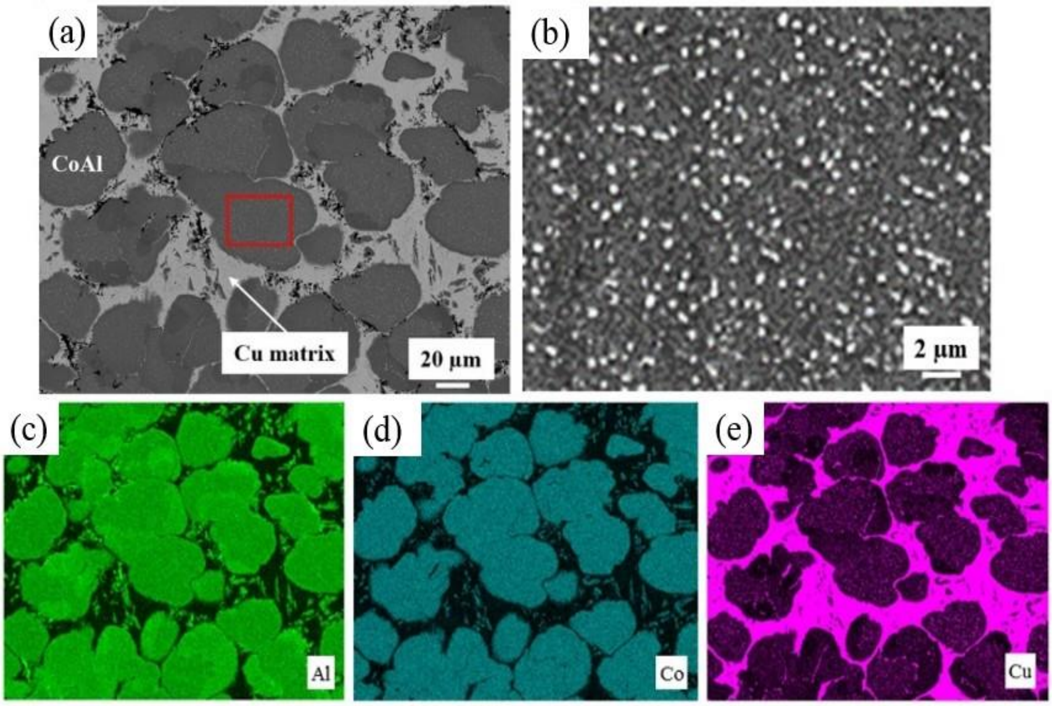

Fig. 3. (a) BSE-SEM image showing the LPSed CoAl (50 wt.%)/Cu composite, (b) high-magnification BSE-SEM image of the box area in (a) highlighting the Cu sub-micrometre sized precipitates inside the CoAl reinforcement particle; (c), (d) and (e) are the Al, Co and Cu elemental EDX maps, respectively.

The presence of sub-micrometre sized CoAl precipitates in the Cu matrix and solid solution of the Cu matrix also increase the HV by 30% from 101, in the Cu matrix of the SSSed sample, up to 132 (see Table 2). The rod-like morphology of the CoAl precipitates suggests the volume diffusion-controlled continuous growth mechanism (see Fig. 5). From the practical point of view, SHS followed by LSP processing can be considered as a cost-effective and efficient route to produce high performance MMCs reinforced with different aluminides.

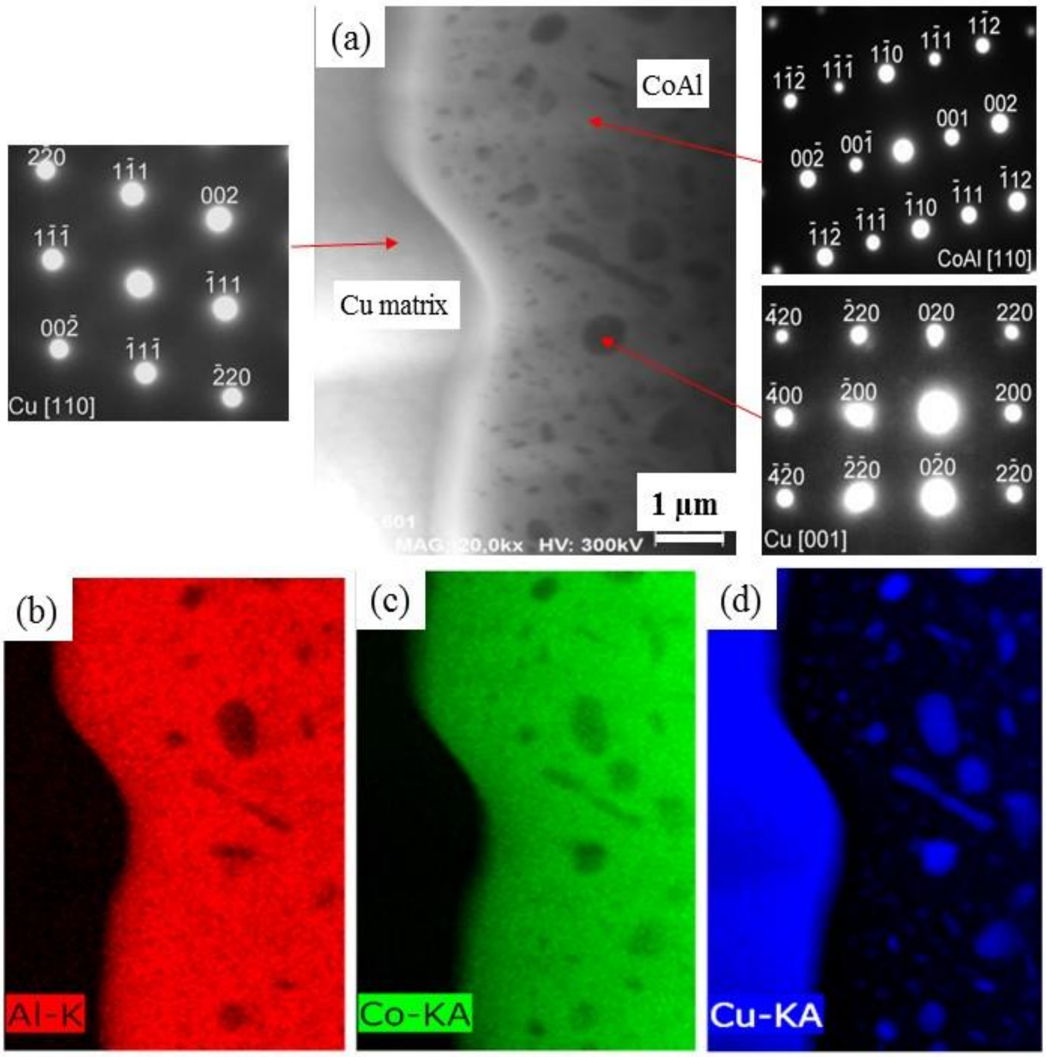

Fig. 4. (a) Bright-field (BF) scanning TEM (STEM) image of the CoAl/Cu interfacial area in the LPSed composite, (b), (c) and (d) are corresponding Al, Co and Cu EDX elemental maps, respectively. The different phases in (a) are indexed by zone-axis spot pattern using microdiffraction.

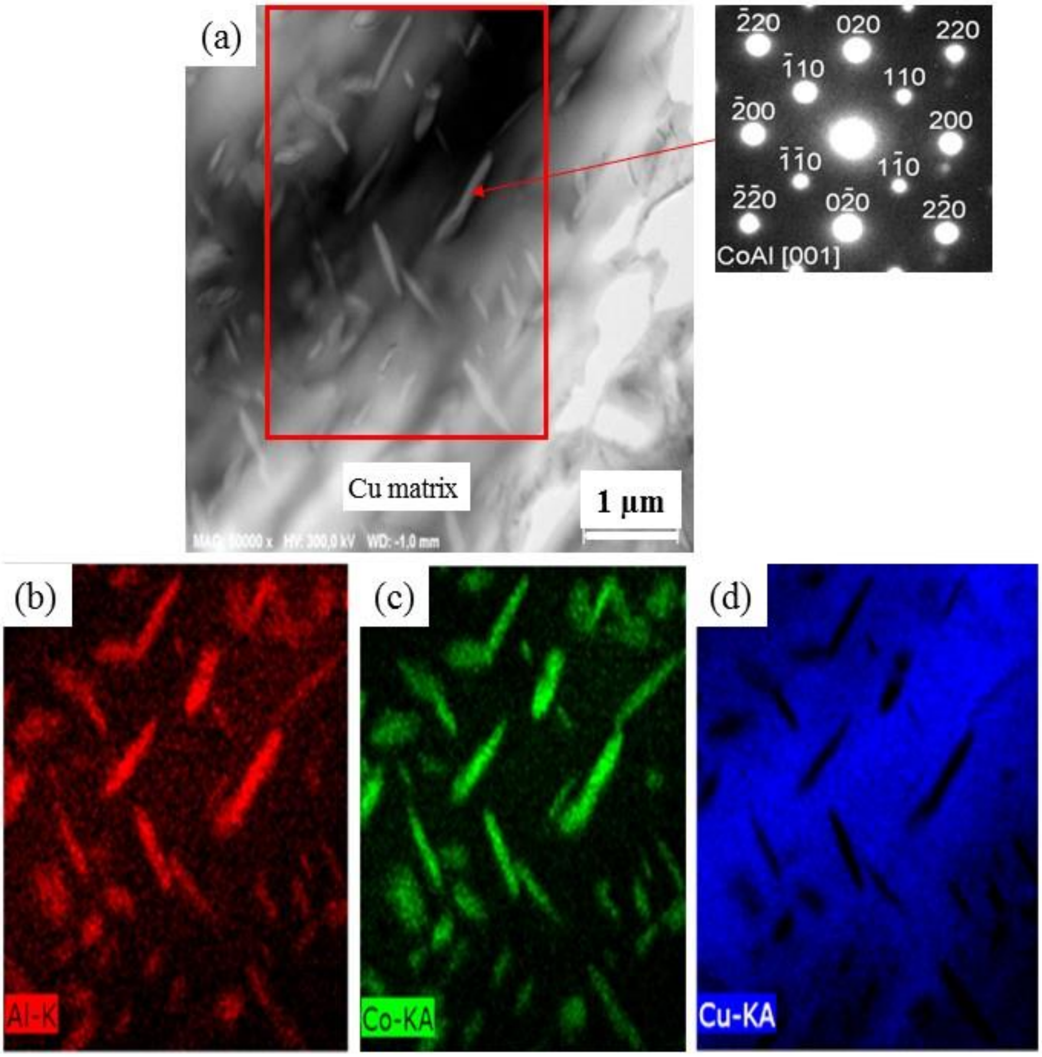

Fig. 5. (a) BF-STEM image showing the rod-like CoAl precipitates in the Cu matrix of the LPSed composite; (b), (c) and (d) are corresponding Al, Co and Cu EDX elemental maps in the rectangle box in (a), respectively. The CoAl precipitates in (a) are indexed by zone-axis spot pattern using microdiffraction.

Finally, it is worth mentioning that interface of any MMCs and, in particular, those reinforced with sub-micrometre and nano-sized reinforcement particles play an important role in determining the overall mechanical and functional properties of the MMCs. The ideal interface (or interface affected area) should serve as the bridge for effective load transfer and/or energy exchange between the matrix and reinforcements. Hence, interface characterization and tailoring are always of great interest in the community of MMCs. In our case, in addition to the interface between the integrated CoAl reinforcement particles and Cu matrix, the formed dispersed precipitates in the CoAl reinforcements and Cu matrix give rise to two new types of interfaces in the LPSed composite. Configurations of all these three types of interfaces, including interfacial reaction products, bonding states etc., will be systematically studied in our future work.

4. Conclusions

The highly-dense CoAl (50 wt.%)/Cu composites are sintered by SSS and LPS where the porous and single-phase CoAl compound powder synthesized by SHS is used as the reinforcement phase. Multiscale microstructure characterization has been carried out by XRD, SEM and TEM. It is found that in the LPS process both sub-micrometres sized dispersed precipitates are formed in the CoAl reinforcements and Cu matrix. The Cu particles within the CoAl reinforcement originate from the capillary action on the molten Cu. The LPSed composite presents higher relative density and microhardness (measured both in the CoAl reinforcements and Cu matrix) than those of the SSSed one. The increase of microhardness is attributed to full densification of the CoAl reinforcements, precipitation of CoAl in the Cu matrix and solid solution of the Cu matrix.

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