

MICROSTRUCTURE AND PHYSICAL PROPERTIES OF BLENDED AND COATED (Ta, Nb)C/Ni CERMETS

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Abstract

Mixed and coated (Ta, Nb)C/Ni cermets are produced by the powder metallurgy route. The applied Ni content of present cermets is 5%, 10% or 15% Ni. Samples are compacted at 400 MPa and sintered at 1450 °C for 90 min. X-Ray Diffraction, SEM and ADEX analysis are used to study the microstructure. Physical properties such as saturation magnetization, electrical conductivity, and thermal expansion are also studied. It is observed that saturation magnetization, electrical conductivity and thermal expansion of mixed and coated samples increase with nickel content. Thermal expansion of coated samples is lower than those of mixed samples. However, mixed samples exhibit higher physical properties than coated samples. Besides this, the presence of phosphorus and silver in coated samples significantly affects their physical properties.

Keywords: powder metallurgy; (Ta, Nb)C/Ni cermets; blending; electroless Ni deposition; microstructure; magnetic; electrical and thermal expansion properties.

INTRODUCTION

Refractory metals such as tantalum, niobium, titanium, molybdenum, tungsten, and vanadium are used to produce cutting tools by the powder metallurgy route. Such materials are sintered at very high temperatures. Sometimes, external pressure is simultaneously applied to obtain dense material. In order to reduce the processing temperature and to improve the mechanical properties, metallic binders such as Co, Ni and Cr are added to ceramics to form composites called cermets [1, 2]. Cermets are technically ceramic particles bonded with a metal; hence “cer” for ceramic and “met” for metal [5]. Cermets offer a good compromise between hard brittle ceramic particles and the ductile and tough metallic binder. The advantages of cermets are the high hot hardness which allows high cutting speeds, and the chemical stability which effects high wear resistance and better resistance to oxidation as well as the good surface quality of the workpiece during metal machining built up edge formation [3–6]. Sintering of cermets is usually carried out in the presence of liquid-phase at 1400–1500°C [1].

Cermet materials are widely used in the production of cutting tools used in the machining of steels and gray cast-iron [7-11]. Also, a tool made from cermets is recommended for dry cutting, to withstand the temperature increase to high values.

Tantalum carbide and niobium carbide are characterized by high hardness, high melting point, high chemical stability, good resistance to chemical attack and thermal shock, excellent oxidation resistance and corrosion resistance, excellent electronic conductivity and catalytic activity [11-13]. These particular properties make them find a

wide range of industrial applications. They are usually used to make cemented carbide cutting tools [14]. TaC increases bending strength due to the formation of a complex high strength carbo-nitride phase [15]. It also has a positive effect on resistance to plastic deformation [16]. On the other hand, NbC increases deformation resistance at high temperatures [17].

Nickel has high hardness, excellent chemical and mechanical stability at a broad range of temperature, low density, low thermal expansion and high stiffness [18-19]. In a number of cases, the base metal powders may be coated by another chemical species instead of mixing it by binder materials. The purpose may be to produce a homogeneous mixing and to impart better compressibility during compaction.

Electroless coating is a chemical reduction process, which is based on a catalytic reduction of a metallic ion in aqueous solution containing a reducing agent, and a subsequent deposition of the metal without using electrical energy [20]. Coating processes are grouped as Ni-P, Ni-B or pure Ni according to the reducing agents used (i.e., hypophosphite, borohydride or dialkyl aminoborane and hydrazine, respectively) in the coating bath [21]. The coating procedure consists of three well-known stages: sensitization, activation and metallization [22].

J. Rams et al. [23] show that electroless nickel coating of carbon fibers enhances their wettability, allowing homogeneous distribution of fibers in the matrix and reducing the micro-segregation in the fibers' surroundings. Also, Daoush et al. [24] indicate that the coating process gives a strong interfacial bonding between Al_2O_3 short fibers and Ni particles. Electroless nickel coating is of a uniform thickness, so that it is applied on micro and nano-size particles [20, 25].

The purpose of the present work was to study the physical characteristics of (Ta, Nb)C cemented carbide mixed with different percentages of Ni powder and to compare them with those of (Ta, Nb)C cemented carbide coated with similar percentages of Ni by electroless process, followed by a powder metallurgy route involving cold compaction and vacuum sintering.

EXPERIMENTAL PROCEDURE

Materials

(Ta: Nb) C/90:10 powders of 2-3 μm particle size were supplied by Hermann C. Starck Co, Germany, and nickel powders of 2 μm particle size were purchased from Aldrich Co. for electroless coating process of high purity nickel(II) chloride hexahydrate, ammonium hydroxide, ammonium chloride, potassium sodium tartrate, sodium hypophosphite and silver nitrate were purchased from Algomhoria Chemical Co. Cairo Egypt.

Powders Mixing

(Ta, Nb)C and Ni powders were used to prepare three cermet samples containing 5, 10 and 15 wt% Ni. Also, to reduce friction during compaction, 0.5 wt% paraffin wax was added.

Powder Coating

Metallization of (Ta, Nb)C Particles

The electroless nickel coating process is preceded by two main operations, i.e. modification and activation. Modification includes treatment of surfaces of (Ta, Nb)C

particles to eliminate organic and non-organic materials. For non-organic materials, 10 g of (Ta, Nb)C powders are stirred in 100ml sodium hydroxide solution for 1 hour. For organic materials, the same powders are stirred in 100ml acetone for 1 hour. Then the powders are dried at 100 to 120°C for 30 min.

(Ta, Nb)C is non-conductive. To coat the surface of the particle powders by electroless nickel process, surfaces of 10 g of (Ta, Nb)C powders are activated by adding 2.5 g silver to 100 ml water, and pH value is adjusted to 11.2. Then, 30 ml formaldehyde is added to the solution. After ending the activation process, the solution is dumped and the powders are washed with distilled water. Finally, the powders are dried at 60°C for 60 min.

Coating process

Activated powders were chemically coated with nickel by electroless nickel process. Table 1 shows the chemical composition of the bath used. After the solution pH value reached 9.2 and the temperature reached 92°C, sodium hypophosphite was added and the reaction was immediately started. The composition was adjusted to prepare 4 samples containing 0, 5, 10 and 15 wt% Ni.

Tab.1. Electroless bath chemical composition.

NiCl ₂ ·6H ₂ O	100g/l
NH ₄ Cl	50g/l
Potassium sodium tartarate	80g/l
Sodium hypophosphite	100g/l
pH	~9.2
Temperature	~92°C

Powder Characterization

D8 XPORT X-Ray diffraction device was used to investigate the crystal structure, phase composition, and Lattice parameters of mixed and coated powders. Also, Scanning Electron Microscope (SEM) model Quanta FEG250 was used to investigate the microstructure, shape and size of powders.

Powder Compaction and sintering

A uniaxial hydraulic press was used to compact the powders at 400 MPa. Then, compacted samples were sintered in a vacuum furnace at 1450°C for 90 min under 10⁻² torr. As shown in Fig.1, the heating rate was 2°C/min up to 450°C, and was raised to 5°C/min up to 1450°C. During heating, the temperature was held at 250°C for 30 min to dry the samples from any moisture content. Also, the temperature was held at 450°C for 30min to get rid of gases implanted inside pores. Moreover, to realize liquid phase sintering, the temperature was held at 1450°C for 90 min with dwell times of 30 min at 1000°C. Finally, the furnace was turned off and sintered samples were cooled using a water cooling system for 8 hr.

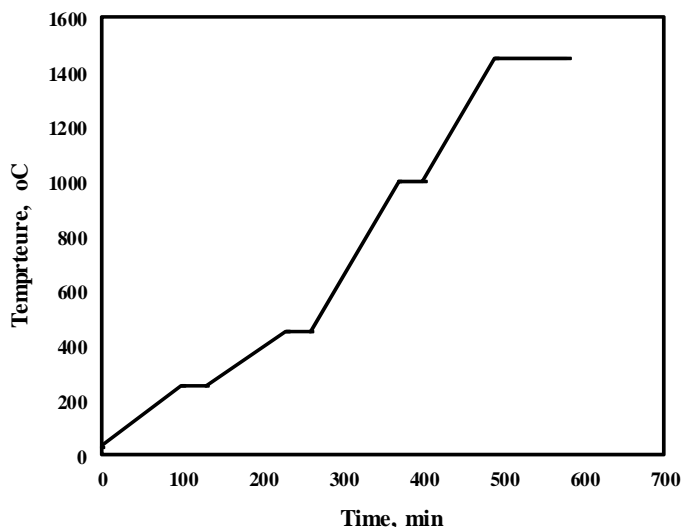


Fig.1. Heating cycle for vacuum sintering.

Measuring Equipment

The density of sintered samples was measured by using the Archimedes method. Silicon carbide SiC papers with 400, 600 and 1200 grit were used to grind and polish the samples. Then, the microstructure was investigated by Optical Microscope and Scanning Electron Microscope. Hysteresis loops, and saturation magnetization were measured by a vibrating sample magnetometer (VSM) model Lakeshore-7400 under 2T magnetic field perpendicular to the Z-axis of samples. Also, the electrical resistance was measured using a Multimeter Digital Bench MX553, then the electrical resistivity was calculated using eq. (1):

$$\rho = \frac{R * A}{L} \Omega cm \quad (1)$$

where, ρ is the electrical resistivity $\Omega.cm$, R is the resistance of material Ω , A is the cross section area of the sample, and L is the thickness. The electrical conductivity σ is the inverse of electrical resistivity.

A digital indicator, glass rod, glass tube, a backer of steel and holder were used to measure the coefficient of thermal expansion (CTE). As shown in Fig.2, the sample was inside a glass tube, and a glass rod and a Digital Dial Gauge were put on it. The sample was heated for 15min at different temperatures. The following equation was used to calculate the thermal expansion coefficient.

$$\alpha = \frac{1}{\Delta T} * \epsilon \text{ } ^\circ C^{-1} \quad (2)$$

where, $\Delta T = T - T_0 \text{ } ^\circ C$, $\epsilon = \Delta L / L$, and $\Delta L = L - L_0 \text{ mm}$

and α is the coefficient of thermal expansion $1/^\circ C$, T is the furnace temperature, T_0 is the absolute temperature, ϵ is the strain, L is the height of the sample after heating, and L_0 is the height of the sample before heating.

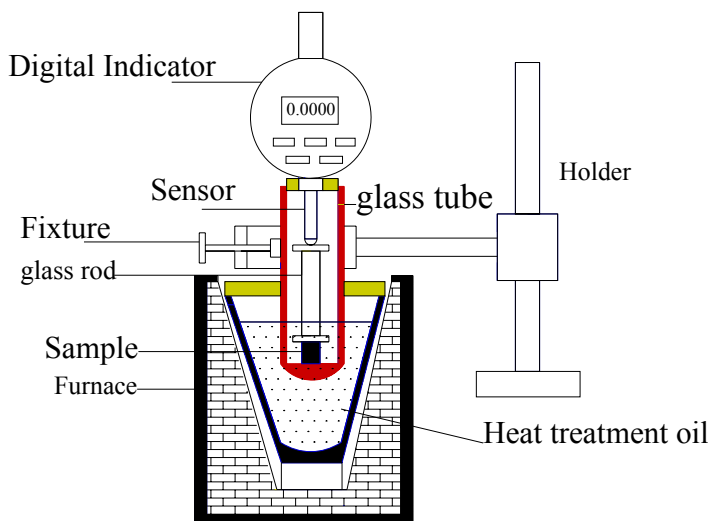


Fig.2. Schematic diagram of the coefficient of thermal expansion measurement rig.

RESULTS AND DISCUSSION

Powder Investigations

SEM/BSE micrographs of coated and mixed (Ta, Nb)C-15%Ni powder samples are shown in Fig.3a and Fig.3b. It is obvious from Fig.3a that (Ta, Nb)C powders are coated by Ni deposited by the electroless process. Besides this, Fig.3b shows that there is no adhesion between (Ta, Nb)C and Ni in mixed powders. Also, Fig.3b shows some accumulations of (Ta,Nb)C.

SEM and EDAX analysis of (Ta, Nb)C-15%Ni coated powders are shown in Fig.3c. The elements comprising it (Ta, Nb)C-15%Ni are Tantalum, Niobium, carbon, nickel, phosphorus, silver and oxygen. It is also observed that the powders contain high silver and phosphorus contents. The presence of Ag is due to the silver activation process carried out before the coating process, while phosphorus is brought from sodium hypophosphite used as a reducing agent in the electroless Ni process.

Figure 4, shows XRD patterns for pure Ni, as well as mixed and coated (Ta, Nb)C-15%Ni. There are nickel peaks, double carbide peaks (Ta, Nb)C, and silver peaks. It is observed that pure Ni and Ta-Nb carbide are fcc phases. Moreover, peaks of deposited Ni (amorphous) are lower than those of pure Ni. This may be due to the presence of up to 4 wt.% P, that leads to the deposition of β -phase ferromagnetic nickel film. Increasing P content to 11 wt.%, the structure changes to non-magnetic γ -phase [26]. Osaka et al. [27] show that P content has a significant effect on the crystallites of Ni, and that increasing P content decreases Ni crystallites.

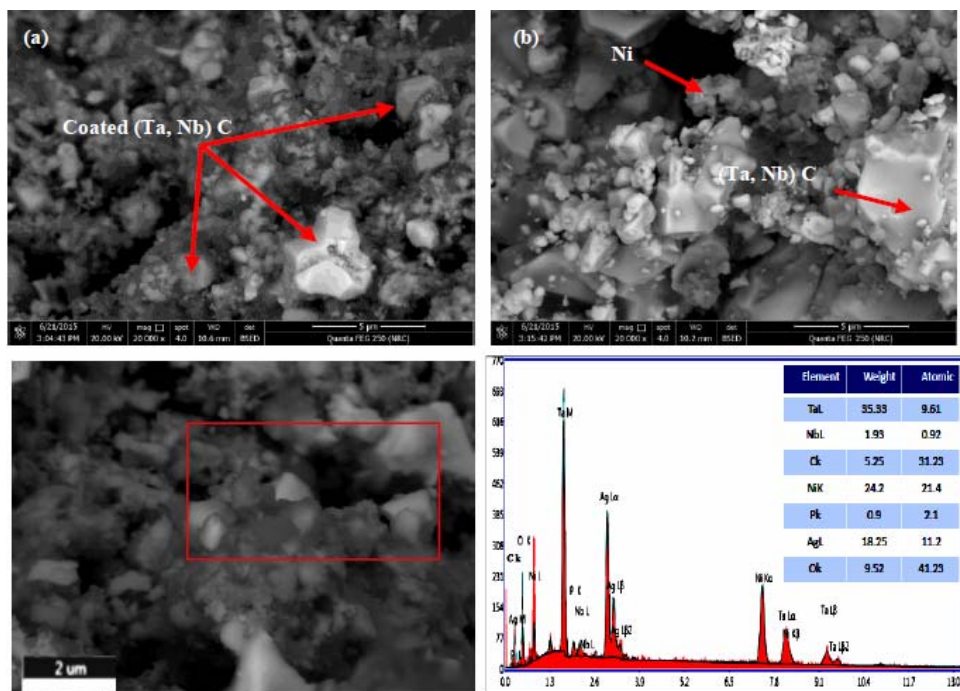


Fig.3. SEM/BSE Micrograph for (a) coated (Ta,Nb)C- 15%Ni powders (b) mixed (Ta,Nb)C-15%Ni powders, and (c) the EDAX analysis for the same coated powders.

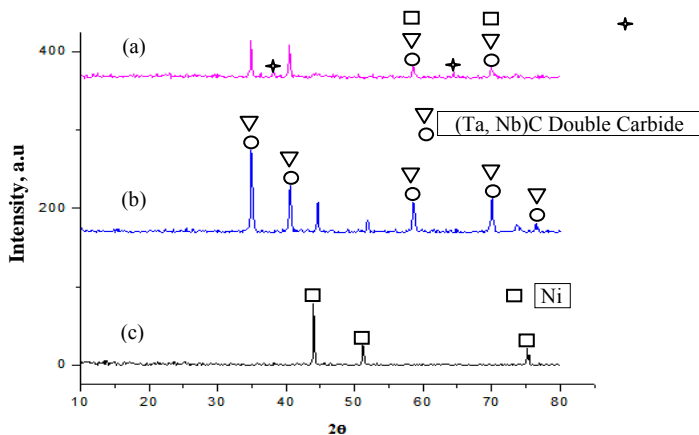


Fig.4. XRD patterns of pure Ni, mixed (Ta, Nb)C-Ni, and coated (Ta, Nb) C-Ni.

MICROSTRUCTURE OF COATED AND MIXED SINTERED SAMPLES

Figure 5 shows SEM photos, BSE mode for sintered coated and mixed samples with different nickel contents. It could be noted that mixed and coated samples exhibit homogeneous distribution of (Ta, Nb) C in nickel, however, mixed samples exhibit some agglomeration of (Ta, Nb) C. Besides this, adhesion is formed at (Ta, Nb)C and Ni interface. The grain size of mixed samples is smaller than that of coated samples, this may be due to mixed powders being subjected to crushing during mixing.

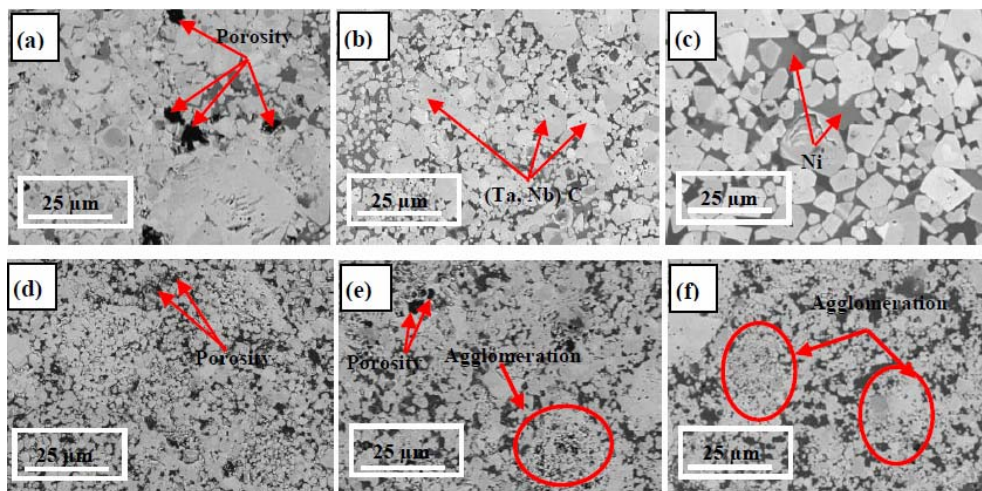


Fig.5. SEM micrographs of mixed and coated (Ta, Nb) C /Ni sintered materials; where (a) (Ta, Nb) C-5 wt. % Ni, (b) (Ta, Nb) C-10 wt.% Ni, (c) (Ta, Nb) C-10 wt.% Ni mixed samples, and (d) (Ta, Nb) C-5 wt% Ni, (e) (Ta, Nb) C-10 wt% Ni and (f) (Ta, Nb) C-10 wt.% Ni coated samples.

Magnetic Properties

The hysteresis loops of mixed and coated (Ta,Nb)C-Ni sintered samples are shown in Fig.6a and Fig.6b. The saturation magnetization M_s of all samples is measured at 2T magnetic field and at room temperature. It is worth noting that the saturation magnetization of sintered pure Ni is 53.3 emu/g, and for deposited Ni it is 36.

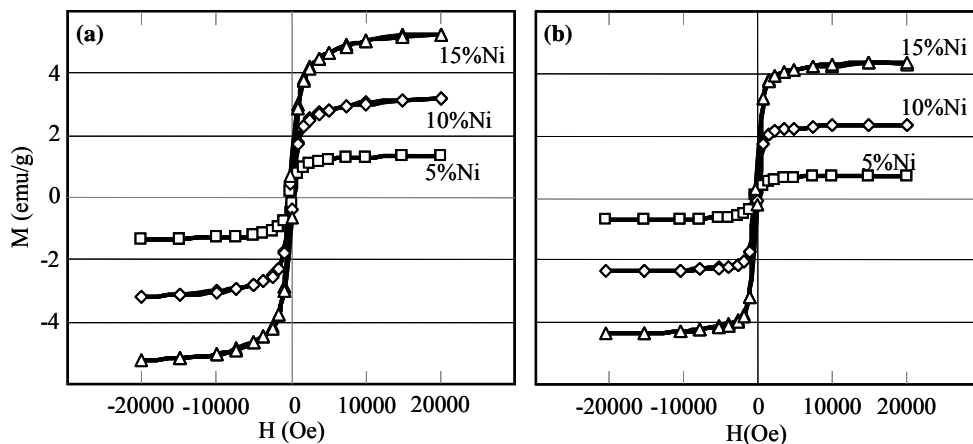


Fig.6. H-B hysteresis loops of sintered samples of: (a) Mixed (Ta, Nb) C/Ni, and (b) Coated (Ta, Nb)C/Ni containing different nickel contents at 2T.

Figure 7 shows the effect of Ni content on the saturation magnetization M_s for mixed and coated samples. It is obvious that M_s values increase with Ni content in both cases. For coatings containing 15% Ni, the M_s of mixed samples (5.24 emu/g) is higher than that of

coated samples (4.31 emu/g). The presence of P in the deposited nickel layer affects the magnetic properties of coated samples of (Ta, Nb)C-15wt% Ni. The magnetic properties of EN coating has been studied [26, 27], and it has been shown that increasing phosphorus content decreases the saturation magnetization of the nickel film deposited. The saturation magnetization of the coated samples is also affected by the presence of silver [28].

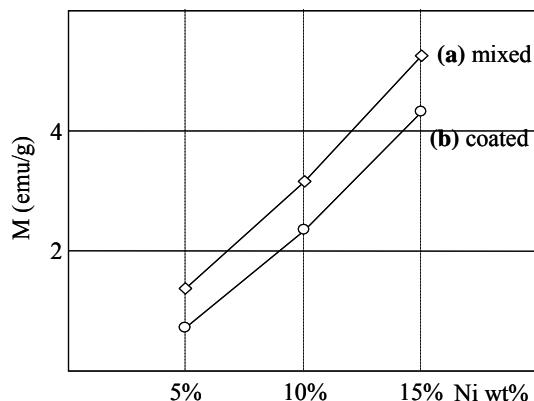


Fig.7. Effect of nickel content on magnetic saturation of mixed and coated (Ta,Nb)C:Ni.

Electrical Conductivity

The electrical conductivity of Ni composites is important, especially if used in electrical, electronic or mechanical applications that require conductive cutting tools such as the electro-chemical grinding machine, and the electric discharge machine. The electrical conductivity is then affected by the conductive phase in the composite.

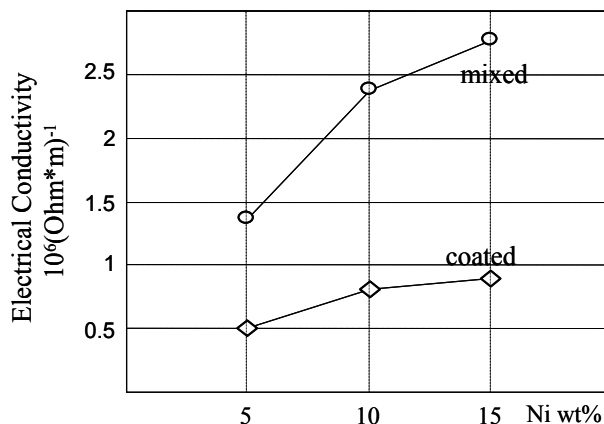


Fig.8. Effect of Ni content on electrical conductivity of mixed and coated sintered (Ta, Nb)C/Ni.

The effect of Ni content of sintered mixed and coated (Ta, Nb)C-Ni cermets is shown in Fig.8. The electrical conductivity increases with Ni content for mixed and coated samples. It is higher for mixed samples than for coated samples. This could be due to the presence of phosphorus in nickel film deposited by the electroless Ni process. Phosphorous

hinders the movement of free electrons [29]. Phosphorous atoms are trapped between Ni atoms and reduce the possibility of contact between nickel atoms [30].

Thermal Expansion

The thermal expansion coefficient of mixed and coated samples at various temperatures for 15 min holding time is shown in Fig.9. It is shown, that the coefficient of thermal expansion CTE of coated and mixed samples increases with Ni content and with temperature. CTE of coated samples is lower than that of mixed samples, probably due to the presence of phosphorus.

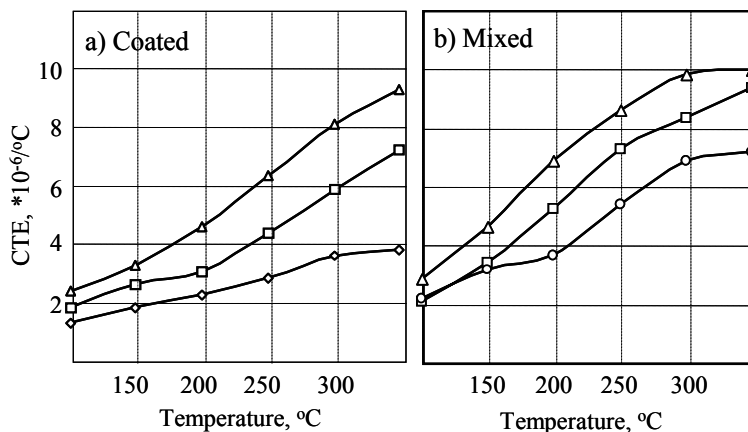


Fig.9. Coefficient of thermal expansion CTE vs. temperature for coated and mixed (Ta, Nb)C/Ni.

CONCLUSION

Based on present results, it could be concluded that:

- Mixed and coated samples are compacted under a pressure of 400 MPa and then sintered at 1450°C for 90 min.
- The XRD pattern of coated (Ta, Nb) C shows that the crystallite of deposited nickel is may be amorphous.
- The SEM of coated powders using electroless process shows that tantalum niobium carbide powders are coated by nickel. The mixing process shows a homogeneous distribution of the powders' constituents. However, no adhesion between particles could be observed.
- Mixed samples exhibited some agglomeration of (Ta, Nb) C.
- H-B hysteresis loops of mixed and coated samples show that the magnetic saturation of mixed samples is greater than that of coated samples. This may be due to the presence of phosphorous and silver. The electrical conductivity also shows a similar trend.
- The measured value of the coefficient of thermal expansion of coated samples is lower than that of mixed samples.

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