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Interface Study for the Design of Alternative Matrixes in Cermets

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Abstract

Liquid Phase Sintering (LPS) is used in the fabrication of hard materials and cermets which are difficult to densify by other approaches. During this process the melting point of the metal matrix is reached and the solid reinforcement is soluble in it. Thereby, via rearrangement and solution-precipitation mechanism, these composite materials are sintered obtaining high density, hardness and wear resistance.

For this sintering mechanism it is very important to know the solubility and wetting behavior at high temperature of the metallic matrix and the reinforcement. In recent years one of the research topics in the field of hard materials is the search for new metallic matrixes so it becomes mandatory to study its interaction with the reinforcement from the viewpoint of solubility and wettability. This work shows a study combination of simulation tools and experimental testing of contact angle measurement at high temperature of the system Ni/TiCN because Ni is the conventional metallic matrix used in cermets and it is compared with the systems Fe/TiCN and Fe-15Ni/TiCN because the Fe is the main candidate for an alternative metallic matrix.

1. Introduction

Nowadays one of the main topics of current research in the field of hard metals and cermets is the development of alternative metallic matrixes to conventional ones which have in their composition Ni and/or Co [1]. The preferred substitute is Fe because of its similarity in chemical structure, its safety, low cost and ability to be hardened by heat treatment [2]. There have been several works using Fe as a metallic matrix and the results have been very satisfactory [3, 4] for this reason it is necessary to study in depth the Fe/TiCN system.

The processing of these composite materials is performed by Liquid Phase Sintering (LPS). This processing method is called LPS because the melting temperature of one component is reached. Depending on the solubility between liquid phase and solid phase there are two types of LPS: *Persistent*, when the solid is soluble in the liquid and the liquid presents a low solubility in the solid, and *Transient*, when the liquid is soluble in the solid but disappears after forming [5]. Even though the solubility between phases is a determining factor in the success of the LPS process [6, 7], one also has to consider another factor that is closely related to the solubility: the wettability between both phases.

The wetting behavior is studied by the contact angle (θ) measurement and it is determined by the relation of surface energies of liquid, solid and vapor, according to the Equation 1.

$$\gamma_{sv} - \gamma_{sl} = \gamma_{sv} \cos \theta \quad \text{Equation 1}$$

If there is no solubility or reaction between the liquid phase and the solid (*inert system*) the wetting behavior will only be determined by their surface energies. If the liquid phase reacts with the solid (*reactive system*) a new phase will form at the interface and that this will determine the wetting behavior. If the liquid phase dissolves the solid (*dissolutive system*) the composition of the liquid phase will be altered during the residence time at high temperature and thus vary the surface energy of the liquid. In this case the contact angle is given by the new surface energy and the substrate dissolution [8]. These three wetting types are shown in Figure 1.

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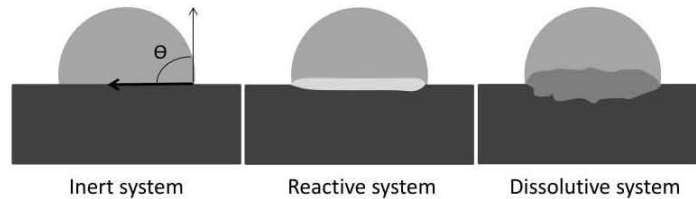


Figure 1. Wetting types depending on solubility and reactivity between liquid sample and solid substrate.

In the case of cermets the LPS is persistent and the liquid metal and the ceramic reinforcement form a dissolutive system. Their sintering mechanism takes place in several steps: 1) The liquid metal wets the solid ceramic particles, 2) the ceramic particles are partially dissolved by the liquid metal and 3) the solid particles reprecipitate around undissolved solid particles enriched in elements from the liquid phase [9].

In this sintering mechanism is very important to know the interaction, in terms of solubility and wettability, between metallic matrix and ceramic reinforcement at high temperature in order to choose the proper alternative matrix. This work is a deep study of the interaction between the conventional metallic matrix, Ni, the main alternative metallic matrix, Fe, and a combination of both, Fe-15Ni, and the TiCN ceramic reinforcement using the combination of simulation tools and experimental testing of contact angle measurement at high temperature.

2. Materials and methodology

The powders used as starting materials in this work are: TiCN (H. C. Starck), Fe (Ecka granules), Prealloyed Fe-15Ni (H. C. Starck) and Ni (INCO T-110).

The simulation of high temperature solubility at the interface between the metal and TiCN reinforcement is performed by using the software DICTRA with the TCFE7 database. The design of the system used in the simulation is shown in Figure 2. There are two regions, the left one corresponds with the liquid metal sample and the right one corresponds with the solid TiCN. The simulated distance is 1000 μm and the simulation times are 1, 10, 100 and 1000s. The temperature at which each simulation has been performed has been chosen in order to have the metal in liquid state. The T simulation of the Ni/TiCN system is 1500 $^{\circ}\text{C}$ because the melting point of the pure Ni is 1455 $^{\circ}\text{C}$ and the T simulation of Fe/TiCN system is 1550 $^{\circ}\text{C}$ because the melting point of the pure Fe is 1538 $^{\circ}\text{C}$.

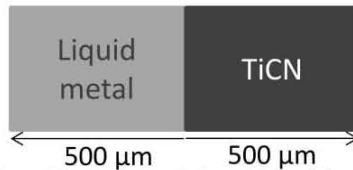


Figure 2. Scheme of the system designed for the simulation of the diffusion at the interface between the metal sample and TiCN substrate.

The equilibrium phase diagrams shown in this work have been calculated using ThermoCalc software [10]. Calculations are based on the free Gibbs energy minimization code and mass conversion rule, in combination with TCFE7 and TTNI7 databases (Scientific Group Thermodata Europe).

To study the wettability of metal samples and TiCN ceramic reinforcement wetting experiments at high temperature have been performed. These experiments were conducted in a tube furnace under Ar atmosphere. The furnace is provided with a camera, which through a window records the evolution of the shape of the drop of liquid metal on the TiCN substrate. So the evolution of the contact angle between the two phases with the residence time and temperature is monitored by the sessile drop method.

The metal samples were previously sintered under vacuum atmosphere at 1450 $^{\circ}\text{C}$ during 1 hour. The TiCN substrates were sintered by Spark Plasma Sintering at 1900 $^{\circ}\text{C}$ and a pressure of 70 MPa with a heating and cooling rate of 100 $^{\circ}\text{C}/\text{min}$ to a relative density of 99.5 %.

After the wetting experiments, a cross section is made in the system formed by the metal and the ceramic substrate sample to study the interface between the two phases by observation in the Scanning Electron Microscope (SEM).

3. Results

Figure 3 shows the evolution of the contact angle between the liquid metals: Fe, Ni and Fe-15Ni on TiCN substrate with some images taken during the contact angle experiments. The first image corresponds with the starting of the melting of the metallic samples ($t = 0$ s) and the final image corresponds with a residence time of 600 s. The contact angle formed in the system Ni/TiCN ($\theta = 10^\circ$) is lower than the contact angle of the system Fe-15Ni/TiCN ($\theta = 24^\circ$) and much lower than the contact angle of the system Fe/TiCN ($\theta = 64^\circ$).

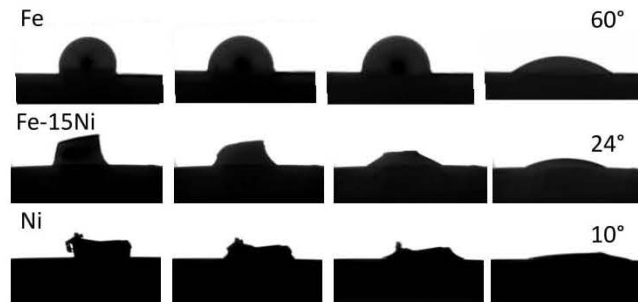


Figure 3. Contact angle evolution of the samples Fe, Ni and Fe-15Ni on TiCN substrate with respect residence time.

To understand the differences found in the final contact angle between these metallic samples and TiCN substrate the evolution of the wetting behavior with the residence time should be studied. Figure 4 shows the evolution of the contact angle with the residence time of the three systems. The wetting behavior of the Fe liquid drop on TiCN is very different from that of the Ni and Fe-15Ni liquid drops. From the beginning of the Fe sample melting the contact angle is 100° and it remains static until 550 s of residence time when it decreases sharply to 64° . The wetting behavior of Ni and Fe-15Ni is quite different because the contact angle formed at the beginning of the sample melting decreases smoothly with the residence time.

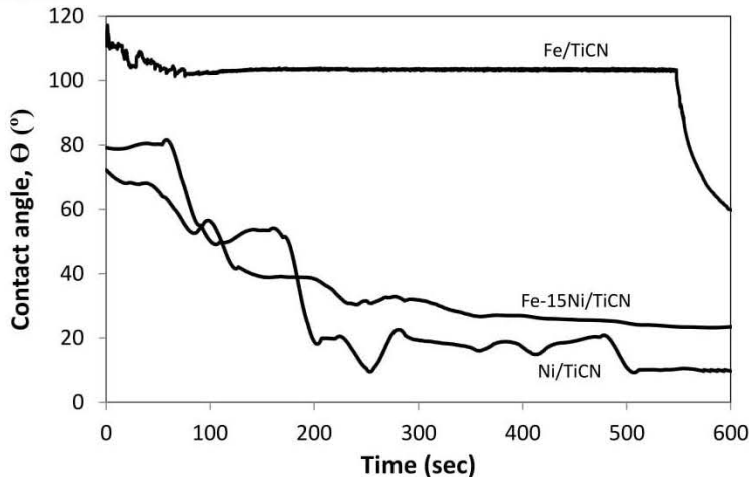


Figure 4. Evolution of contact angle respect time of liquid Fe, Fe-15Ni and Ni on TiCN solid substrate.

The difference in contact angle evolution could be due to the different solubility between Fe and Ni on the TiCN substrate. The solubility between the sample and substrate can be studied by the phase diagram. In Figure 5 is shown the binary phase diagrams of Fe/TiCN and Ni/TiCN. In both diagrams the region in which the liquid phase appears is coloured. This region and, therefore, the solubility of the TiCN in the metallic sample is much higher in Ni than in Fe.

To complete the study of the Ni/TiCN and Fe/TiCN interface the displacement of the interface position with respect to residence time has been simulated and the results are shown in Figure 6. It is observed that there is a slightly higher displacement of the interface in the system with Ni than in the system with Fe. However, the small difference in the displacement of the interface position does not seem to be in accordance with the great difference in solubility of TiCN in Ni and Fe as it has been seen in the phase diagram in Figure 5.

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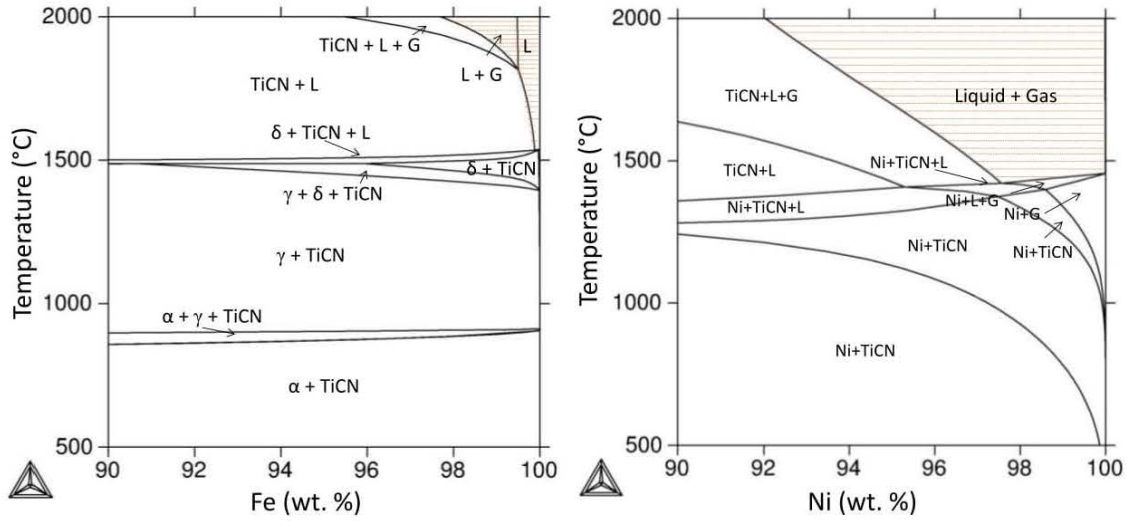


Figure 5. Binary phase diagram of Fe/TiCN (left) and Ni/TiCN (right).

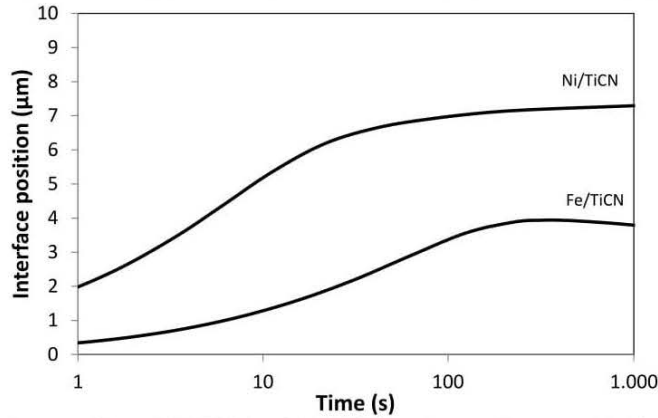


Figure 6. Interface position of Ni/TiCN and Fe/TiCN systems with respect to the residence time.

By observation of the interface formed between the metallic samples and the TiCN substrate after wetting experiments, Figure 7, it is confirmed that the higher solubility of TiCN in liquid Ni than in liquid Fe does not result in the displacement of the interface position but results in the dissolution of the substrate and the infiltration of the liquid Ni between the grains of TiCN.

The interface between Fe and TiCN shows a slight dissolution of the TiCN substrate and forms a interface of 10 μm . The interface formed between Ni and TiCN shows a high dissolution of TiCN substrate and the infiltration of liquid Ni between TiCN grains in 160 μm . The infiltration of the liquid metallic sample in TiCN substrate takes place also in the sample with Fe-15%wt. Ni.

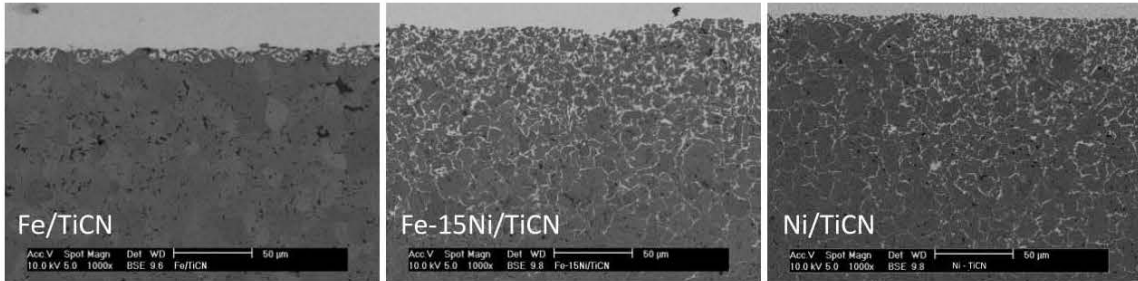


Figure 7. Interface between metallic sample and solid substrate of the systems Fe/TiCN, Fe-15Ni/TiCN and Ni/TiCN after high temperature wetting experiments.

The solubility of TiCN in the metallic sample has also consequences in the temperature of liquid phase formation during the wetting experiment. In Table 1 is shown the melting point and the temperature of the liquid phase formation of Fe, Fe-15Ni and Ni during wetting experiments. It is observed that during the wetting experiment of Fe the liquid phase is formed at 1542 °C which is a similar temperature to Fe melting point, namely, during the experiment its melting temperature is not altered. However when the sample is Ni the formation of the liquid phase takes place 75 °C before the melting point of Ni and in the case of the Fe-15Ni the liquid phase appears 20 °C before its melting point. In both cases the dissolution of TiCN substrate in the metallic sample changes the liquidus temperature. As it can be seen in the equilibrium phase diagram of Ni-C and (Fe-15Ni)-C in Figure 8, an increase of carbon content decreases the liquidus temperature of Ni and Fe-15Ni.

Table 1. Melting point and temperature of liquid phase formation of Fe, Fe-15Ni and Ni.

	Fe	Fe-15Ni	Ni
Melting point (°C)	1538	1498	1455
Liquid phase formation (°C)	1542	1478	1380

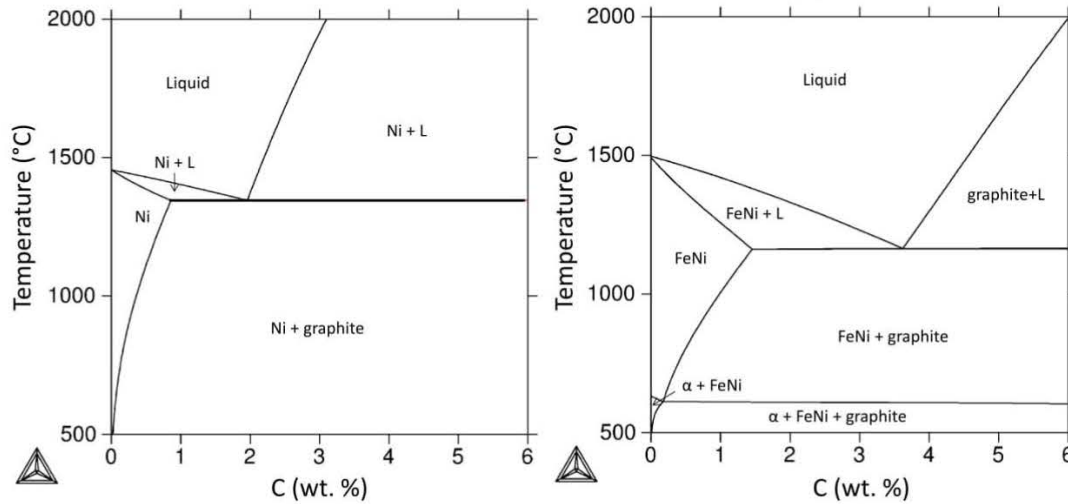


Figure 8. Phase diagram of Ni-C (left) and (Fe-15Ni)-C (right).

4. Conclusions

In this work the wettability of Fe, Ni and Fe-15Ni on TiCN has been studied. To perform the study the high temperature wetting behavior has been tested and the analysis of the results is supported by the study of the solubility between metallic sample and ceramic reinforcement at the interface by simulation and by microscopy observation and calculation of the equilibrium phase diagrams. In view of the results obtained it can be concluded:

- Ni shows higher wettability on TiCN substrate than Fe.
- The high wettability of Ni on TiCN ($\theta = 10^\circ$) is due to the high solubility of TiCN in liquid Ni. It has been observed that the liquid Ni dissolves the TiCN substrate and infiltrates between the TiCN grains.
- Fe does not have wettability and solubility on the TiCN for low residence time. From 550 s residence time the wettability improves slightly ($\theta = 64^\circ$) because of increased the solubility of TiCN in liquid Fe.
- The presence of a small percentage of Ni (15 wt. %) in the Fe sample greatly increases the solubility of TiCN and, therefore, decreases the contact angle between the two phases.

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