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Interface analysis in Al and Al alloys/Ni/carbon composites

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Nature of fibre/matrix interfaces existing in Al/C composites were investigated depending on the presence of a nickel interlayer deposited on carbon fibres and on the composition of the aluminium matrix. Auger and electron microprobe analyses were used. The role of the nickel layer on the chemical evolution of the system after a 96 h heat treatment at 600 °C is discussed. The presence of this nickel layer limits the diffusion of carbon into aluminium, and thereby, eliminates the formation of a carbide interphase, Al_3C_4, which is known to lower the mechanical properties of Al/C composites. The mechanisms differ according to the composition of the matrix. In the case of pure aluminium, an Al-Ni intermetallic is formed after thermal annealing. It does not react with the carbon fibre and so inhibits the growth of Al_3C_4. In the case of the alloyed matrix (AS7G0.6), the dissolution of the Ni sacrificial layer, after annealing, does not lead to the same Al-Ni intermetallic but a thin nickel layer remain in contact with the carbon fibre avoiding formation and growth of Al_3C_4 carbide. This difference of behaviour is tentatively ascribed to the presence of silicon that segregates at the fibre/matrix interface.

1. Introduction

Aluminium/graphite composites are promising composites for structural applications due to their high specific properties [1]. However, the elaboration of such composites by infiltration of molten aluminium into carbon fibre preforms undergoes three major difficulties: (1) a lack of wetting of the fibre with the molten aluminium, (2) a deterioration of the fibre properties during composite processing and (3) the formation of brittle reaction products between the fibre and the matrix. To overcome these difficulties, coatings can be deposited on fibres by various methods such as electroless deposition, electroplating, vapour deposition and plasma spraying [2]. Nickel, copper and gold are the three main surface coatings used for carbon fibres in metal matrix composites. They are chemically stable with carbon and can be deposited by electrochemical or chemical methods.

Because most metal matrix composites can be regarded as non equilibrium systems during their preparation and their high temperature service, a gradient of chemical potential exists at the fibre/matrix (F/M) and fibre/coating/matrix interfaces. This difference in chemical potential provides the driving force for diffusion and/or chemical reaction when the composites are heated to elevated temperatures [3].

It has been shown that metallic coatings deposited on carbon fibres helps the infiltration by the molten aluminium of unidirectional preforms (decrease of applied squeeze casting pressures) [4]. Gold and copper coatings also reduce the formation of undesirable Al_4C_3 compound at F/M interfaces after different heat treatments [5]. However, no chemical investigation has been performed on the other possible metallic coating, i.e. nickel. So, in order to consider its use in Al/C composites, the interfacial reactions occurring at Al/C and at Al and Al alloy/Ni/C interfaces, were determined in non-annealed and annealed composites. The composition of the phases formed at the interface, under controlled conditions, were analysed using electron probe micro analysis (EPMA) and auger electron spectroscopy (AES) line scan profiles.

2. Experimental

2.1. Preparation of composites

Composites were obtained by a squeeze casting process which is one of the most important casting methods presently used [6, 7]. The matrix were either pure aluminium or aluminium alloy containing 7 at. % silicon and 0.6 at. % magnesium (AS7G0.6). The T700 carbon preforms, consisted of either uncoated or coated fibres. The nickel coating was realised according to an electrochemical technique which is essentially based on the dipping of the fibre preforms in three successive baths (sensitisation, activation and coating) [8]. The first two steps took place at ambient temperature while the third one was realised at 65 °C. The chosen experimental

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conditions allowed a dense 0.5 μm nickel film to be deposited on the carbon fibres. The Al or AS7G0.6 liquid matrix at 800 °C was poured into the preform which was preheated at 450 °C. This procedure was carried out in an ambient atmosphere. The pressure applied to the system were up to 100 MPa. After cooling, ingots with approximate dimensions of $70 \times 40 \times 40$ mm^3 were obtained.

2.2. Analysis methods

Ingots were cut using a diamond saw and subsequently polished to a mirror finish for EPMA observations. The microprobe used was a Camebax with a lateral resolution of 0.5 μm and the AES data were acquired on a VG-MICROLAB 310-F Microprobe with a lateral resolution of 20 nm. Analyses conditions were an accelerated voltage and beam current of 10 keV and 1 nA, respectively. The data were recorded in the conventional EN(E) mode. The energy range investigated in this multiplexing technique were the following for each element: O: 495–515 eV, Al: 1375–1405 eV, Ni: 800–870 eV, C: 250–275 eV, and Si: 1595–1620 eV. The peak identification was determined by reference to an EAS data base [9] or from reference compounds analysed in the same apparatus. In many cases, peak overlap or small changes in chemistry make the chemical analysis of a multicomponent mixture difficult. So, a specific procedure was followed to analyse a set of spectra obtained by line profiles in order to plot the atomic concentration of each element versus the point position in the line, in respect to its chemical state. Data acquired at different position across the sample are computer-analysed using numerical methods applied to the matrix data. Non Linear Least Square Fitting (NLLSF) was the well known technique used during this work.

3. Results and discussion

3.1. Fibre/matrix interface analysis in Al/C composites

Fig. 1 shows a AES line scan profile across the interface of a non-annealed Al/C composite (reference sample). Three regions can be observed: (i) on the left side of the figure, the aluminium matrix, (ii) in the middle part, an interface zone where carbon, aluminium and oxygen are present and (iii) on the right side, the carbon substrate. Fig. 2 shows the same type of interface after a long thermal treatment (600 °C for 96 h). Aluminium matrix and carbon substrate are still present on the sides of the figure. But now the interface zone is modified as shown by the different shapes of the curves corresponding to the atomic concentration of Al and C. It has to be mentioned that the oxygen content does not increase with annealing time and temperature and therefore the influence of this species is not considered in the following. The change of the interface zone is attributed to the formation of Al_3C_4 which results from the dissolution of carbon and its subsequent diffusion into the aluminium matrix.

As a general concern, the formation of Al_3C_4 must be prevented, first because it is associated to a degradation and a decrease of the diameter of the carbon fibre and second because of the fragile nature of Al_3C_4.

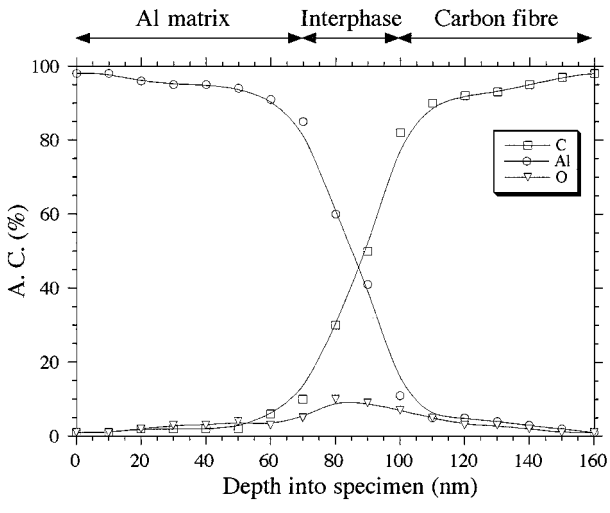

Figure 1 AES line scan profile across the F/M interface for an as-fabricated Al/C composite.

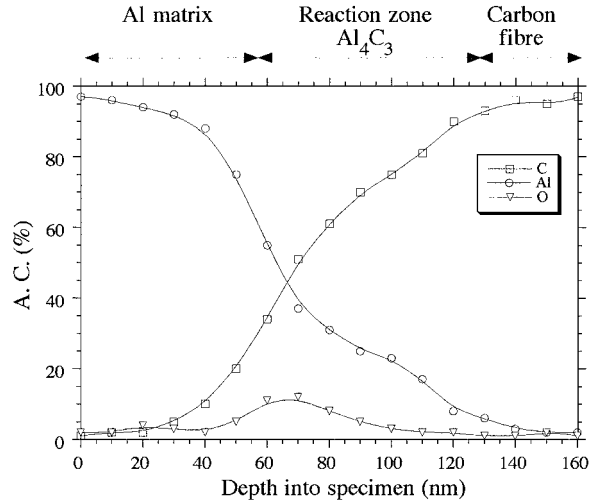

Figure 2 AES line scan profile across the F/M interface for an Al/C composite, annealed at 600 °C for 96 hours.

3.2. Fibre/matrix interface analysis in Al/Ni/C composites

Fig. 3 shows an AES line scan profile across the F/M interface for a non-annealed Al/Ni/C composite (as

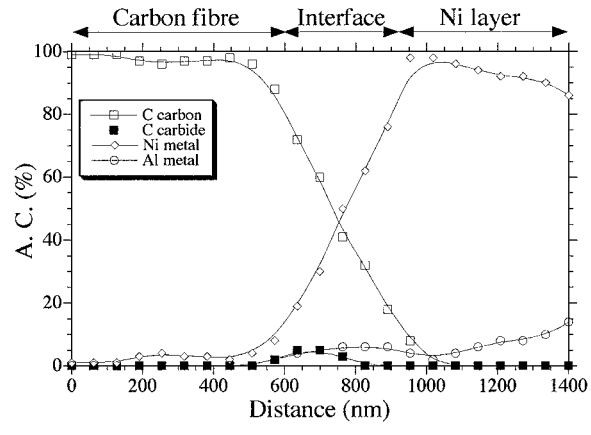

Figure 3 AES line scan profile across the F/M interface for an as-fabricated Al/Ni/C composite.

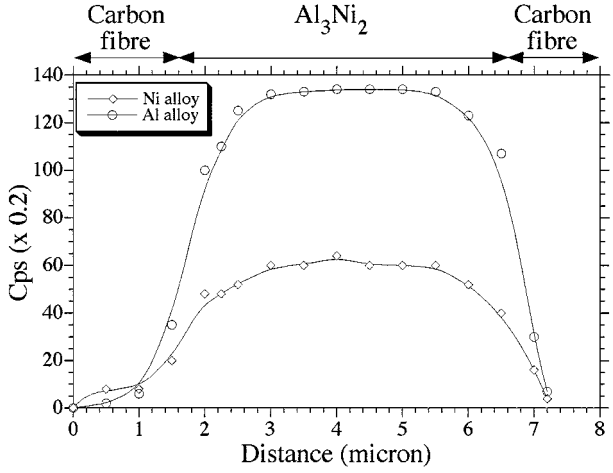

Figure 4 EPMA line scan profile across the F/M interface for an Al/Ni/C composite, annealed at 600 °C for 96 hours.

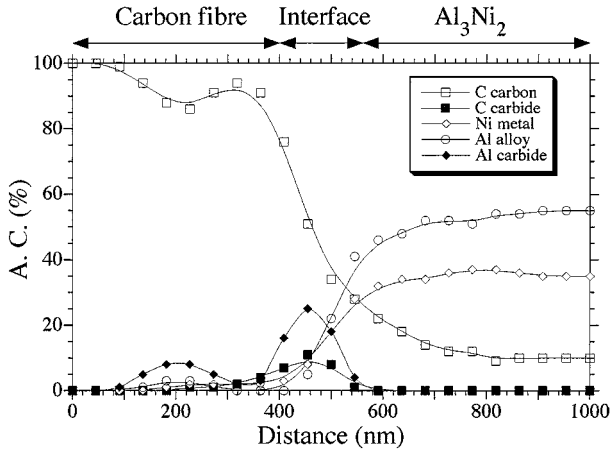

Figure 5 AES line scan profile across the F/M interface for an Al/Ni/C composite, annealed at 600 °C for 96 hours.

obtained by the squeeze casting process). In fact, due to the thickness of the nickel layer (around 0.5 μm) and due to the length of the performed scan (1.4 μm), only the interface between C and Ni is presented (the aluminium matrix does not appear on the current figure). Three regions can be observed: (i) on the left side, the carbon fibre containing a small concentration of metallic nickel and aluminium, (ii) in the middle, a narrow interphase zone (500 nm) constituted of C, Ni, Al and a carbide compound and (iii) on the right side, the nickel layer containing a low concentration of aluminium (around 10 at %). Out of the scale on the right side, the Al matrix is present and only constituted of aluminium.

The evolution of the Al/Ni/C interface was investigated after composite annealing at 600 °C during 96 h. Fig. 4 gives an EPMA line profile of that interface area. This analysis shows that the nickel layer is no more present but instead gave rise in between carbon fibres to a Al-Ni alloy, presenting a defined composition. In order to obtained more precise information on the distribution of the phases across the C/Al-Ni alloy interface, AES analyses were performed on a zone like the left part of Fig. 4 (cf. Fig. 5). The NLLSF treatment indicated the presence of two types of aluminium species, one associated to the Al_3C_4 intermetallic and another one associated to a Al-Ni alloy. Two types of carbon were also identified, one related to Al_3C_4, the other one corresponding to pure carbon (fibre) while nickel was associated to the Al-Ni alloy. These phases were distributed in three area (Fig. 5). The left part corresponds to the carbon substrate containing a low amount of aluminium carbide (Al_3C_4). The narrow middle interface zone (200 nm) corresponds to the Al_3C_4 intermetallic. The right part appeared mainly constituted of the Al-Ni alloy as already observed using EPMA. The quantitative determination of the Al/Ni ratio is close to that of Al_3Ni_2 alloy which is also known to be the most thermodynamically stable intermetallic compound of the aluminium-nickel system [10].

The presence of a very small amount of Al_3C_4 in the non annealed composite (cf. Fig. 3) can actually be noticed. But, in fact, this is likely due the presence of local discontinuities of the nickel layer which enable the aluminium liquid matrix to be in contact with the carbon fibre during processing of the composite. The low aluminium concentration present inside the nickel layer can also be associated to these defects in the initial nickel layer (or may be related to polishing contamination). Now, the important point to be underlined is that the Al_3C_4 amount observed at interfaces of annealed composites (Fig. 5) is not significantly higher than that of the as-prepared materials. So, the formation and the growth of Al_3C_4 which should take place during thermal treatment at 600 °C is highly reduced compared to a Al/C composite (i.e. without interfacial nickel layer). The sacrificial nickel layer prevented or limited the formation of Al_3C_4: the nickel layer does not act directly as a diffusion barrier against carbon but leads to the formation of a stable Al-Ni intermetallic compound by diffusion of nickel in the aluminium matrix during heat treatment. Then, the Al-Ni compound inhibits further diffusion of carbon toward aluminium matrix and prevents the formation of the undesirable Al_3C_4 compound.

3.3. Fibre/matrix interface analysis in AS7G0.6/Ni/C composites

3.3.1. Non annealed sample

Fig. 6 presents a scanning electron microscopy (SEM) image of a section of a non-annealed AS7G0.6/Ni/C composite and the corresponding Al, Ni and Si EPMA maps. Taking into account the EPMA accuracy (0.5 μm^3 resolution), several features relative to the distribution of the minor elements of the alloy in the composite can be given. On one hand, the distribution of silicon within the matrix is non homogeneous. Bright spots clearly reveal the segregation of silicon. On the other hand, nickel looks homogeneously distributed around the carbon fibres. The nickel layer thickness is close to 0.5 μm. Moreover, the circular shape of carbon fibres suggested that no degradation occurred during preparation of this composite.

Fig. 7 gives the AES line scan of the interface between one of these fibres and the surrounding matrix. The numerical NLLSF treatment indicated the presence

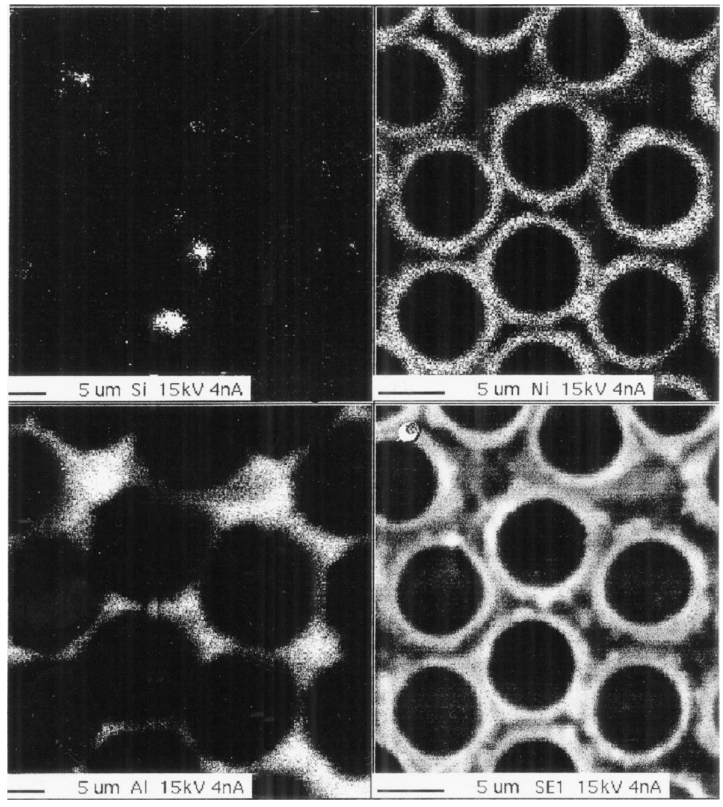

Figure 6 Large area EPMA map for an as-fabricated AS7G0.6/Ni/C composite. a) SEM micrograph of the scanned area, b) Al disribution map, c) Si disribution map, d) Ni disribution map.

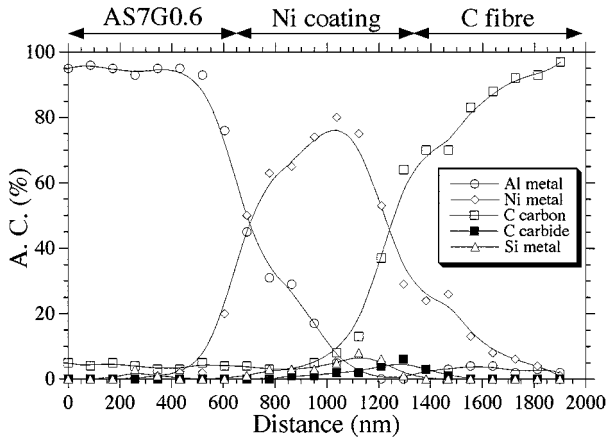

Figure 7 AES line scan profile across the F/M interface for an as-fabricated AS7G0.6/Ni/C composite.

of one type of aluminium species (metallic aluminium), two types of carbon species ($C_{Al_3C_4}$, C_{fibre}) and only one silicon and one nickel species. As previously observed, the interface may be divided in three zones corresponding to the aluminium base matrix, the nickel layer and the carbon fibre from the left side to the right side of the figure.

Small amounts of impurities are present in these area. In particular, a very small amount of carbide can be identified in the intermediate nickel layer close to the Ni/C interface. This carbide can be associated with a small silicon segregation. Considering these NLLSF results obtained on a non-annealed composite, the absence of sharp interfaces (like the ones observed for the Al/C sample) is not attributed to chemical reaction but is rather associated to polishing artefact and/or roughness of the nickel coating.

3.3.2. Annealed sample

Fig. 8 shows a SEM micrograph of a section of a AS7G0.6/Ni/C composite annealed at 600 °C during 96 h together with the corresponding Al, Ni and C EPMA maps. The silicon signal was low which did not allow to obtain a significant map. Aluminium and nickel appeared well distributed in between carbon fibres. The diameter of these fibres appears unmodified compared to the non-annealed composite and the regular aspect of the F/M interface (at that scale) suggests that the thermal annealing did not induce a degradation of the fibres.

The AES line scan of the F/M interface is presented in Fig. 9. The numerical NLLSF treatment just showed simple chemical environment (element-element) for the different species. The interface is still divided in three regions: the aluminium based matrix is observed on the left side of the figure and the carbon fibre on the right side. The thickness of the interphase area is reduced compared to the non annealed sample (Fig. 7) and this region does not correspond any more to a well defined nickel layer: a low amount of nickel and a segregation of silicon are observed.

As for the Al/Ni/C composite, the absence of formation of the Al_3C_4 carbide at the F/M interface was observed for the AS7G0.6/Ni/C composite. During the annealing procedure, Ni can diffuse inside the AS7G0.6 matrix to form an Al rich-Ni solid solution. The low nickel content observed inside the matrix is in agreement with the low nickel solubility given by the Al-Ni

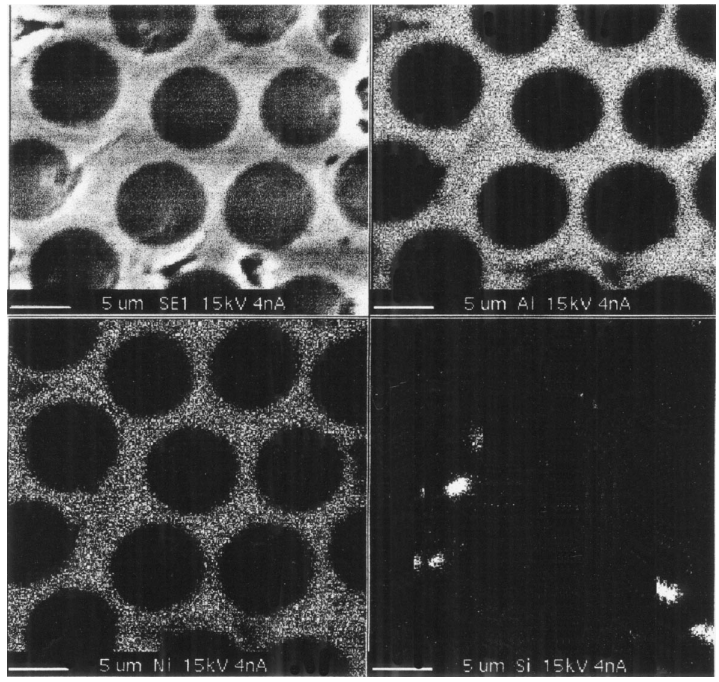

Figure 8 Large area EPMA map for an AS7G0.6/Ni/C composite annealed at 600 °C for 96 h. a) SEM micrograph of the scanned area, b) Al disribution map, c) Ni disribution map, d) C disribution map.

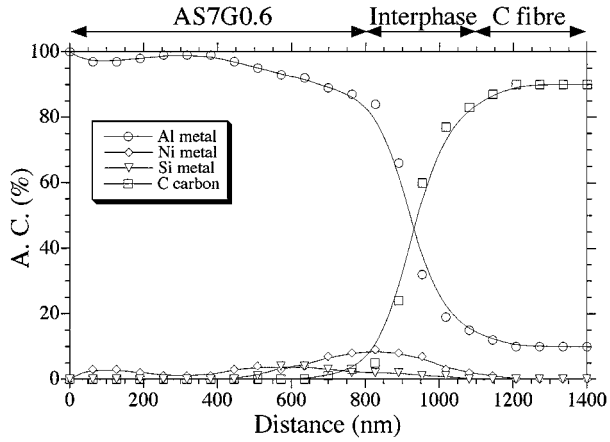

Figure 9 AES line scan profile across the F/M interface for an AS7G0.6/Ni/C composite, annealed at 600 °C for 96 hours.

phase diagram [10]. It is not presently understood why such an Al rich-Ni solution is formed in the case of the AS7G0.6 matrix instead of the Al_3Ni_2 interphase observed in the case of the pure Al matrix. This may be correlated to the presence of Si and/or Mg in the matrix. Therefore, in the case of the AS7G0.6 alloy, nickel eventually associates with silicon to form some Ni-Si intermetallic at the interface, which limits carbon diffusion into the matrix and thereby avoid Al-C reaction.

4. Conclusion

The present study demonstrates that the presence of a nickel layer in between Al or Al alloy matrix and carbon fibres avoids the formation of a fragile Al_3C_4 compound at F/M interfaces when the composites are heat treated for long time. For the pure aluminium matrix, diffusion of nickel inside the matrix leads to the formation of a stable Al_3Ni_2 compound which inhibits the diffusion of carbon into the aluminium matrix. For the AS7G0.6 matrix, the protection process seems a little different. Nickel also diffuses inside the matrix but no define Al-Ni intermetallic compound is formed which may be ascribed to the presence of alloy additive elements (Si and Mg). However, during the course of that diffusion process, remaining nickel staying at the interface may react with Si to form some Ni-Si intermetallic which could prevents carbon diffusion and dissolution inside the aluminium based matrix and therefore inhibits the formation of Al_3C_4.

Acknowledgement

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References

1. J. P. ROCHER, J. M. QUENISSET and R. NASLAIN, *J. Mater. Sci. Let.* **4** (1985) 1527.
2. K. HONJO and A. SHINDO, *J. Mater. Sci.* **21** (1986) 2043.
3. T. W. CHOU, A. KELLY and A. OKURA, *Composite A* **7** (1985) 201.
4. J. F. SILVAIN, Y. LE PETITCORPS and L. ALBINGRE, *Rev. Metall.* **9** (1994) 1348.
5. J. F. SILVAIN, M. R. TURNER and M. LAHAYE, *Composite A* **27** (1996) 691.
6. Y. ABI, S. HORIKIRI, K. FUJIMURA and E. ICHIKI, in Proceeding of ICCM-IV, edited by T. Hayashi (1982) 1427.
7. T. W. CLYNE and J. F. MASON, *Metall. Trans. A* **18** (1987) 1519.
8. J. COLETO, INASMET (Spain), Private communication (1997).
9. Handbook of Auger Electron Spectroscopy (Physical Electronic Publisher, Eden Prairie, USA, 1978).
10. H. OKAMOTO, *J. Phase Equilibria* **14** (1993) 257.

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