EFFECT OF ADDED Si ON DENSIFICATION OF Ni-Al INTERMETALLIC COATING ON SPHEROIDAL GRAPHITE CAST IRON SUBSTRATES

by Tetsuro Kimata[1]*, Keisuke Uenishi[1], Akira Ikenaga[2], Kojiro F. Kobayashi[1]

[1]Department of Manufacturing Science, Osaka University, 2-1-Yamadaoka, Suita, Osaka, 565-0871, Japan, kimata@mapse.eng.osaka-u.ac.jp
[2]Department of Metallurgy and Material Science, Osaka Prefecture University 1-1 Gakuen-Cho, Sakai, Osaka 599-8531, Japan, ikenaga@mtl.osakafu-u.ac.jp

ABSTRACT

Reaction synthesis is a process to form ceramics, intermetallics and their composites from elemental powder mixture. Application of this process to a surface modification techniques has a possibilities to enable the process at a lower temperature or for a shorter time, although synthesized materials are likely to include voids and unreacted elements. This paper intend to examine the effect of Si addition to the mixture of Al and Ni on the densfication of synthesized Ni-Al intermetallic compounds and to evaluate the surface properties of obtained coatings. By the Si addition, exothermic reaction temperature to form Ni-Al intermetallic was lowered to be below the melting point of Al. Si soluted Al_3Ni_2, Al_3Ni and Al_6Ni_3Si were mainly formed in the coating layer when powder mixture was heated to 973K for 300s. Besides, densification was enhanced by increasing hot press pressure, Si additions and heating rate. When the composition of eutectic Al-Si reaches 78%, void ratio of sintered compact reduced to 0.4%. It is caused by higher flowability of Al-Si liquid phase generated and its infiltration into the void. Since the hardness of NiAl(Si) compound (about 600HV) formed in the coating layer is higher than that of Ni-Al compound (about 400HV), coating layer with high density and superior wear property is obtained by hot press using reaction synthesis from Al-Ni-Si powder mixture.

KEYWORDS

Nickel aluminide(NiAl), coating, reaction synthesis, hot press, cast iron

1. Introduction

Nickel aluminides are promising intermetallic compounds for high temperature structural application because of high specific strength at high temperatures, and good oxidation resistance[1]. On the other hand, spheroidal graphite cast iron (FCD) has many functions like high strength and damping capacity, so it is widely used for the frame of a machine. Recently, improvement of the surface property involving the wear resistance, high temperature oxidation resistance, corrosion resistance is desired to FCD[2]. However, available methods for FCD are limited because of weak adhesion to substrate or heat affection to substrate. Reaction synthesis is known to be one of the powder metallurgical techniques for obtaining intermetallics, ceramics from the mixture of composing elemental powders[3-5]. Application of this process to a surface modification technique has a possibilities to enable the process at a lower temperature or for a shorter time[6,7].

The authors have applied Ni-Al reaction synthesis to the surface modification of FCD with high adhesion between substrate and coating[8-10]. In the previous work[11], Ni-Al intermetallic compound was formed by the reaction synthesis from the elemental mixture of Al and Ni and was simultaneously bonded with the FCD substrate. The coating materials showed good wear resistance. However, the spherical void was introduced in the coating layer. To achieve higher densification, utilization of Al-Si liquid phase formed during reaction synthesis was examined. Compared with the molten pure Al, lower melting point and higher flowability of eutectic Al-Si can be effective to the densification of Ni-Al compound. The purpose of this study is to examine the effect of Al-Si and applied pressure on densification of Ni-Al compound and to produce dense Ni-Al intermetallic coating with superior wear property which is fabricated below the melting temperature of Al.

2. Experimental Procedure

Ni,Al and Si powders with 99.9% purity and average sizes of 3 μm, 3 μm, 3-10 μm respectively, were mixed in the composition of Ni-70at%(Al-12Si), Ni-75at%(Al-12Si), or Ni-78at%(Al-12Si). These powders were die-pressed with a load of 400MPa for 60sec to the disc shape compact of 10mm in diameter and 0.5mm in thickness. The relative density of the compact was 60%. Sintering was performed by hot pressing under a vacuum of 5.0×10^{-2}Pa as shown in Fig.1. The sample was heated at the heating rate of 6.66K/s by a high frequency induction heating equipment and held at the sintered temperatures. The pressure was applied from the beginning of heating and to the end of cooling. When fabricating coating materials, spheroidal graphite cast iron (FCD450) cut into a column of 10.5 $\phi\times$3mm was prepared as a substrate and the surface was cleaned by polishing with alumina and lincing with acetone. The cross section of the sintered material was observed by electron probe microanalysis (EPMA) and optical microscopy (OM). The composition of the intermetallics in the sintered materials was identified by electron dispersive X-ray (EDX) and X-ray diffraction analysis. The reactivity of powder compact was examined by differential scanning calorimetry (DSC) at the heating rate of 1.66K/s under Ar flow atmosphere.

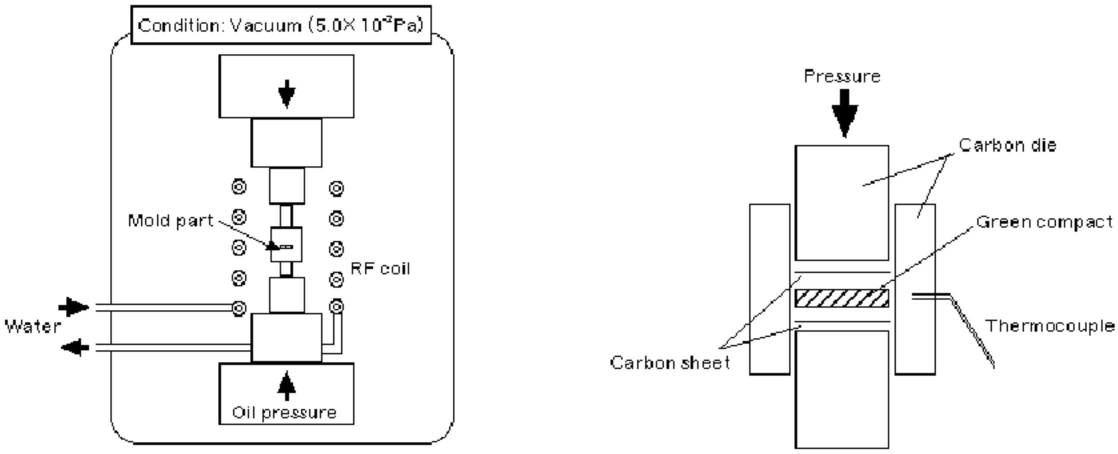


Fig.1 Schematic illustrations of hot press apparatus using high frequency induction heating

3. Results and discussion

3.1 DSC analyses for the combustion synthesis of compact

Figure 2 shows DSC traces obtained when a mixed powder of elemental Ni,Al and Si with a composition of Ni-70(Al-12Si), Ni-75(Al-12Si), or Ni-78(Al-12Si) was continuously heated to 973K at a heating rate of 1.66K/s. The DSC curve showed two exothermic peaks starting from about 850K and from about 910K. These exohtermic reactions occurred below the Al melting temperature (933K)

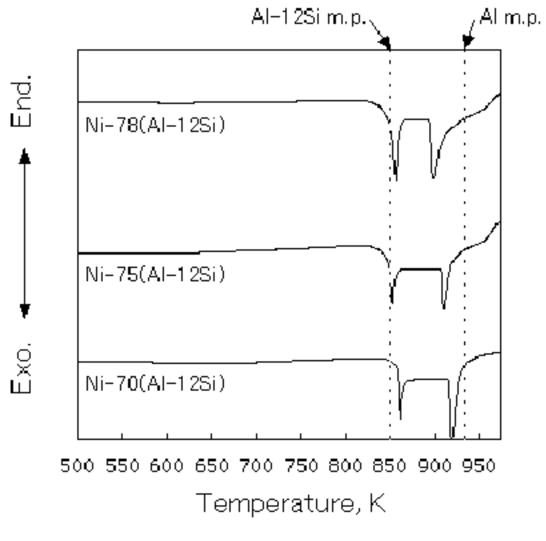
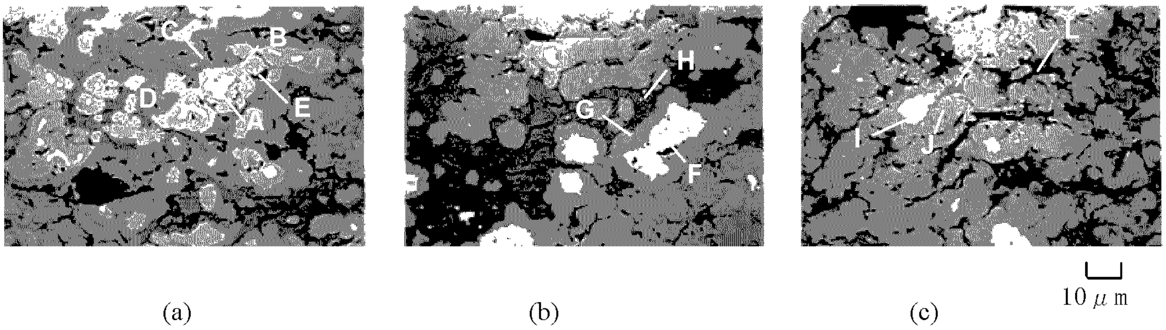


Fig.2 DSC traces of the compact for various composition

3.2 Identification of synthesized compounds

Figure 3 shows the BE (back scattered electron) images of compacts having various composition sintered by hot pressing at 973K for 300s with 7.5MPa. From the results of the quantitative analysis of sintered compact shown in Table1, unreacted Ni (position A) was surrounded by multiple phases which were confirmed to be Al_3Ni_2(Si) for the inner (B) and Al_3Ni and Al_6Ni_3Si for the outer (C,D). The volume fraction of clumpy unreacted Ni decreased with increasing the Al-Si ratio in the green compact and when it reaches 75at%, unreacted Ni was almost consumed by the reaction with Al-Si. For the sample with a composition of Ni-78(Al-12Si), the amount of Al_3Ni_2(Si) decreased and Al_3Ni and Al_6Ni_3Si mainly formed and the dark contrasted phase (L) of Al-Si was dispersed in the compact.



(a) (b) (c)

Fig.3 BE images of compact with a composition of (a) Ni-70(Al-12Si), (b) Ni-75(Al-12Si), (c) Ni-78(Al-12Si) sintered at 973K for 300s with 7.5MPa

Table1 Results of quantitative analysis at each local areas shown in Fig.3

Analysis point	Composition, at.%			Predicted phase
	Ni	Al	Si	
A	99.61	0.39	-	Ni
B	38.05	59.25	2.71	$Al_3Ni_2(Si)$
C	28.44	62.63	8.93	Al_6Ni_3Si
D	23.20	75.65	1.15	Al_3Ni
E	11.66	13.51	74.84	Si rich
F	37.26	55.63	7.11	$Al_3Ni_2(Si)$
G	28.00	62.70	9.30	Al_6Ni_3Si
H	22.84	75.94	1.22	Al_3Ni
I	38.46	55.45	6.09	$Al_3Ni_2(Si)$
J	28.67	61.64	9.70	Al_6Ni_3Si
K	22.31	75.64	2.04	Al_3Ni
L	0.47	18.50	81.03	Al-Si

Figure 4 shows X-ray diffraction patterns of compact having various composition fabricated at 973K for 300s under 7.5MPa. For the sample with a composition of Ni-70(Al-12Si), diffraction peaks of Al_3Ni_2 and Al_3Ni were mainly detected and unreacted Si was also recognized. For the sample with a composition of Ni-75(Al-12Si) and Ni-78(Al-12Si), most peaks were from Al_3Ni but some unknown peaks affirmed. From the quantitative results by WDX, these unknown peak is considered to be from Al_6Ni_3Si.

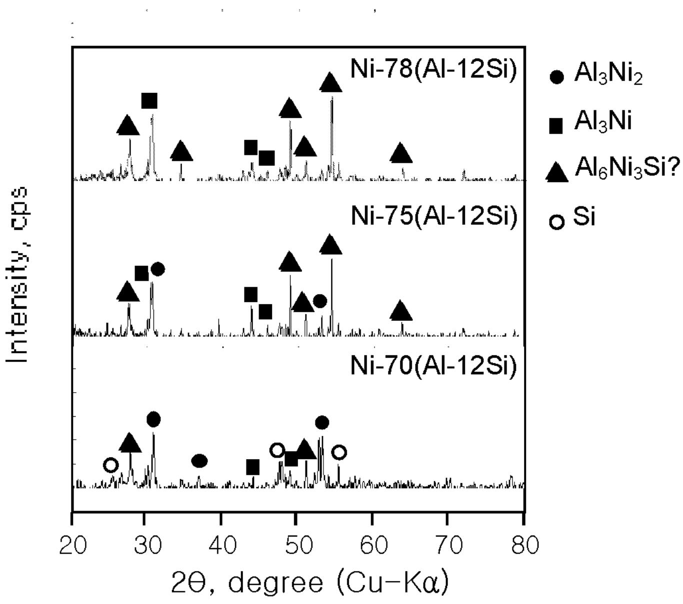


Fig.4 X-ray diffraction patterns of sintered compact with various composition

3.3 Densification behavior of the compacts

3.3.1 Effect of hot press pressure on densification

Figure 5 shows the microstructures of the compact with a composition of Ni-70(Al-12Si) obtained by hot pressing at 973K for 300s under 1, 7.5, 15Mpa respectively. Dark contrasted area is void generated by combustion synthesis. Densification is enhanced by increasing hot press pressure and the void ratio of sintered compact was reduced to 0.72% by applying the pressure of 15Mpa. It was confirmed that application of pressure during sintering can contribute to the densification of Ni-Al compound fabricated by combustion synthesis

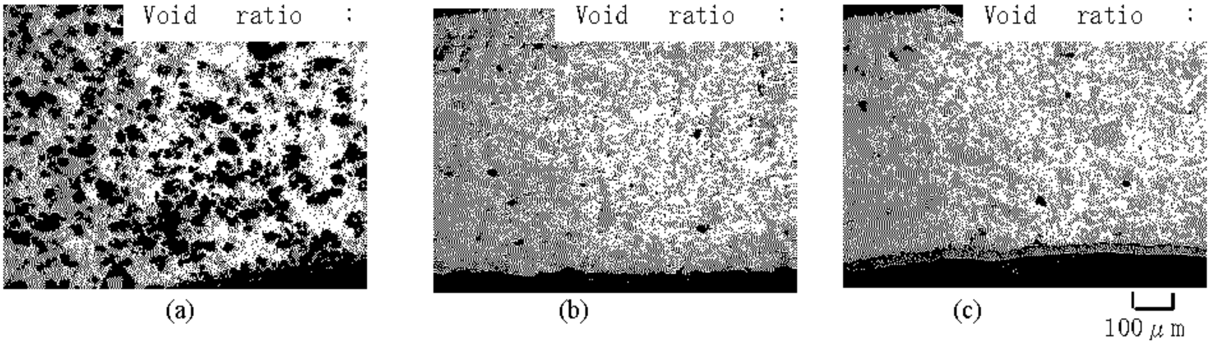


Fig.5 Microstructures of compact fabricated at 973K for 300s with (a) 1MPa, (b) 7.5MPa, (c) 15MPa

3.3.2 Effect of Al-Si addition on densification

Figure 6 shows the microstructures of the compacts with various composition obtained by hot pressing at 973K for 300s with 1MPa and 7.5MPa. Densification was echanced with increasing the eutectic Al-Si ratio. It is considered that when the composition of eutectic Al-Si reaches 75% molten Al-Si well infiltrated into the boundary of each powders. From these results, infiltration effect of molten Al-Si on densification was confirmed even in the lower pressure of 1MPa.

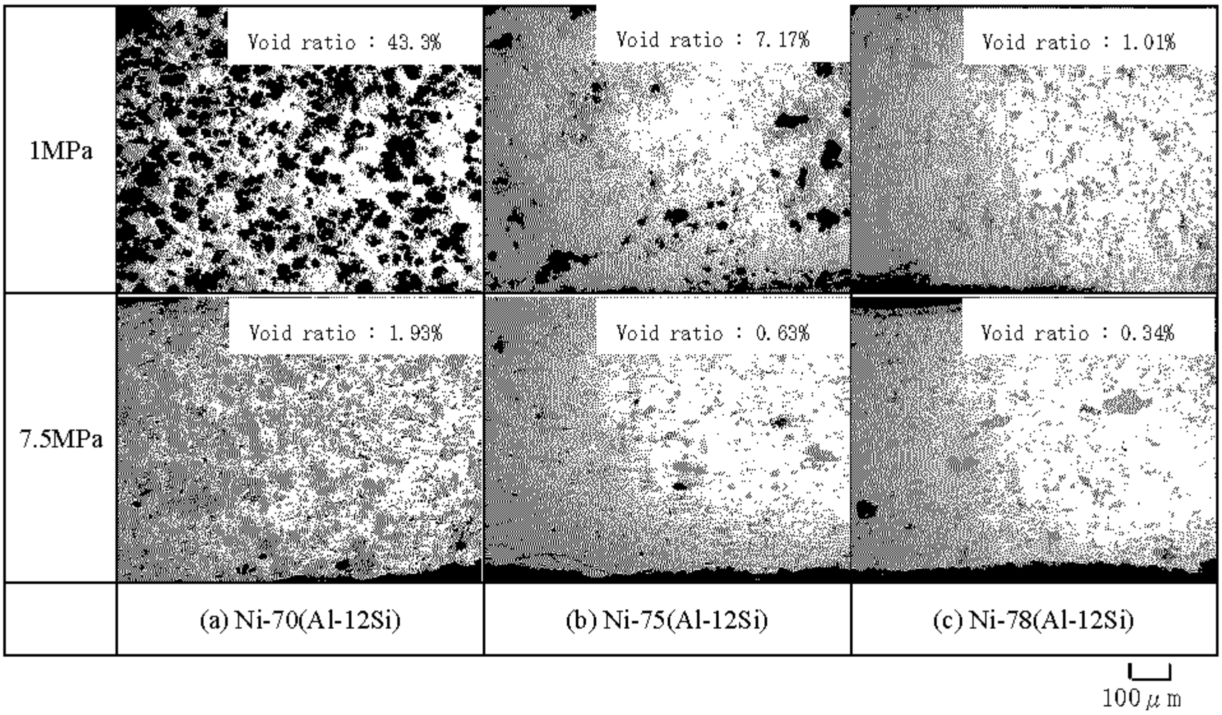


Fig.6 Microstructures of sintered compact with composition of (a) Ni-70(Al-12Si), (b) Ni-75(Al-12Si), (c) Ni-78(Al-12Si)

3.4 Hardness of sintered compacts

Figure 7 shows the Vickers hardness profiles of the sintered compact. The hardness of sintered compact with composition of Ni-70(Al-12Si) were widely scattered ranging from 520 to 740HV at each position. Higher hardness area contains Al_3Ni and Al_6Ni_3Si and lower hardness area contains $Al_3Ni_2(Si)$. Also existence of voids decreases the hardness of samples. The mean hardness increased with increasing eutectic Al-Si ratio and the value was almost constant when eutectic Al-Si ratio reached 75%. It is considered that higher hardness of Al_3Ni and Al_6Ni_3Si mainly formed with composition of Ni-75(Al-12Si) and Ni-78(Al-12Si). Since the mean hardness of the sintered compacts is much higher than that of Ni-Al compound (about 400HV)[12], Ni-Al compound is assumed to be solution hardened by Si solution.

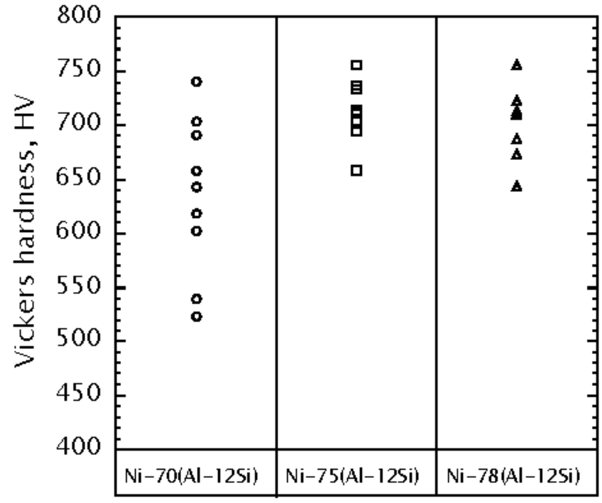
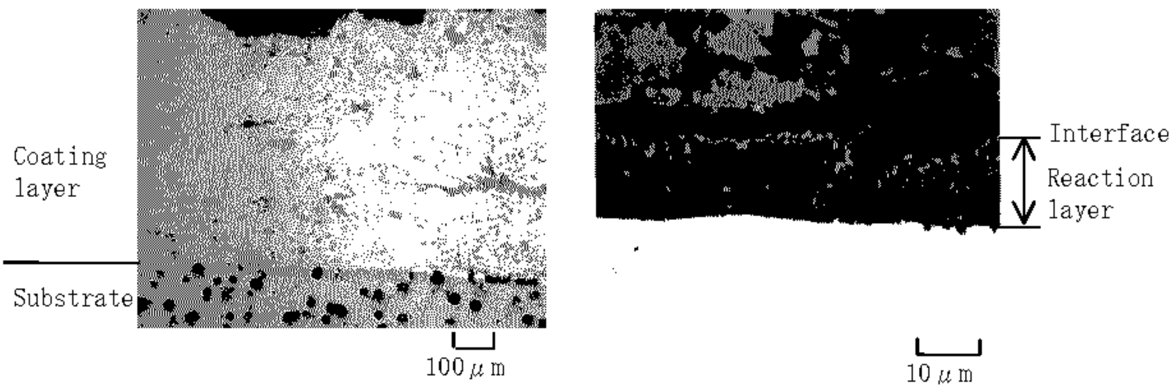


Fig.7 Vickers hardness profiles of the compacts with various composition fabricated at 973K for 300s with 7.5MPa

3.5 Formation of thick coating of Ni-Al compound on FCD substrate

Figure 8 shows the microstructures of the Ni-78(Al-12Si) coating on the FCD substrate obtained by hot pressing at 973K for 300s under 7.5MPa. Dense coating layer was obtained with no delamination. Reaction layer formed in the interface between the coating layer and substrate and the thickness was about 8-10μm. The constituent phase of the reaction layer was identified as $FeAl_3$ by quantitative analysis. This result means that substrate and coating are chemically bonded to retain the sound joint strength.



(a) General view (b) Reaction layer formed on the bonding interface

Fig.8 Microstructure of coating layer fabricated on FCD.

4. Conclusions

Intermetallic Ni-Al(Si) compounds were fabricated by reaction synthesis from an elemental powders mixture and examined the effect of Al-Si and applied pressure on densification of the compounds. In addition, these layers were joined with FCD substrate. The main results obtained are summarized as follows.

1) DSC curve of the Si added Al-Ni-Si elemental powder mixture showed two exothermic peaks starting from about 850K and from about 910K to form Ni-Al intermetallic compound.
2) By reaction synthesis of the sample with the composition of Ni-70(Al-12Si), Al_3Ni_2(Si) and Al_6Ni_3Si mainly formed by hot pressing at 973K for 300s with 7.5MPa. The amount of Al_3Ni_2(Si) decreased with increasing eutectic Al-Si ratio and Al_3Ni and Al_6Ni_3Si mainly formed with composition of Ni-78(Al-12Si). The mean hardness increased with increasing eutectic Al-Si ratio and the value was almost constant about 700HV when eutectic Al-Si ratio reached 75%..
3) Increasing pressure during sintering can contribute to the densification of Ni-Al compound. By applying the pressure of 15MPa void ratio of sintered compact was reduced to 0.72%.
4) Densification was enhanced with increasing eutectic Al-Si ratio from 70 to 78% and when the composition of eutectic Al-Si reaches 78%, void ratio of sintered compact was reduced to 0.4%.
5) Dense Ni-Al intermatallic coating with composition of Ni-78(Al-12Si) was obtained by reaction synthesis of elemental mixture of Al, Ni and Si powder compacts put on FCD substrate.
6) 8-10μm thick reaction layer was formed in the interface between coating layer and substrate and the constituent phase of the reaction layer was identified as $FeAl_3$. This suggests the formation of surface layer strongly bonded with substrate.

References

[1] K.Morsi : *J.Mater.Sci.Eng.A*, 299 (2001) p1-15
[2] *Handbook of Welding and Joining*, (1990), p822
[3] A.G.Merzhanov and I.P.Borovinskaya, *Dolk.Chem.*, 204 (1972), p429
[4] A.Hibino, S.Matsuoka, M. Kiuchi : *J.Mater. proc. Technol.*, 112 (2001), p127-135
[5] A.Biswas, S.K.Roy, K.R.Gurumurthy, N.Prabhu, S.Banerjee : *Acta Mater.* 50 (2002) p757-773
[6] K.Uenishi, T.Matsubara, K.F.Kobayashi : *Z.Metallkd.* 90 (1999) p163-167
[7] P.La, M.Bai, Q.Xue, W.Liu : *Surface and Coating Technol.* 113 (1999) p44-51
[8] A.Ikenaga, Y.Goto, Y.Nitta, M.Kawamoto, K.F.Kobayashi, K.Uenishi : *J.Japan Foundry Eng.* , 68 (1996) , p417-422 (Japanese)
[9] A.Ikenaga, Y.Goto, Y.Nitta, M.Kawamoto, K.F.Kobayashi, H.Araki : *J.Japan Foundry Eng.* , 68 (1996) , p852-857 (Japanese)
[10] A.Ikenaga, Y.Nitta, T.Fujiki, M.Kawamoto, K.F.Kobayashi : *J.Japan Foundry Eng.* , 69 (1997) , p107-112 (Japanese)
[11] T.Kimata, A.Ikenaga, M.Kawamoto and K.F.Kobayashi: Proc. 7th international symposium of the Japan Welding Society (*7WS*), Kobe, November, (2001) p1039-1044
[12] S. Oki, T. Kimata, A. Ikenaga, M. Kawamoto : Proc. 13th Synpo. on Surface Modification Technologies, (*SMT13*), Singapore, October, (1999) p.339-344