J Mater Sci (2010) 45:5158–5163
DOI 10.1007/s10853-010-4246-5

Hot consolidation and mechanical properties of nanocrystalline equiatomic AlFeTiCrZnCu high entropy alloy after mechanical alloying

S. Varalakshmi · G. Appa Rao · M. Kamaraj · B. S. Murty

Received: 27 September 2009 / Accepted: 18 January 2010 / Published online: 24 June 2010

Abstract The present study is aimed to investigate the consolidation behaviour and mechanical properties of nanocrystalline equiatomic AlFeTiCrZnCu high entropy alloy after mechanical alloying. The consolidation was achieved by cold pressing with conventional sintering, vacuum hot pressing and hot isostatic pressing techniques. The microstructure and mechanical properties were evaluated. The hardness and compressive strength of nanocrystalline equiatomic AlFeTiCrZnCu high entropy alloy after vacuum hot pressing are 9.50 and 2.19 GPa and those after hot isostatic pressing are 10.04 and 2.83 GPa, respectively. The wear resistance is found to be higher than the commercially used materials such as Ni-hard faced alloy.

Introduction

According to thermodynamical concepts, solid solutions with simple crystal structures form at the solvent-rich compositions and the ordered intermediate phases form at the centre of the phase diagram. The main problem with multicomponent systems and equiatomic compositions is the anticipated formation of a variety of intermetallics with complex crystal structures, which causes difficulty in processing of these alloys. High entropy alloys (HEAs) are new generation alloys that are based on multicomponent system with equiatomic and/or near equiatomic compositions and form a simple crystal structures due to high mixing entropy [1–3]. According to Boltzmann's hypothesis, the entropy of mixing is maximum at equiatomic compositions. The size factor is an important factor that decides whether the HEAs turn to be crystalline or amorphous [4]. Due to the large solid solution strengthening effect, the HEAs with high hardness offer potential industrial applications, such as tools, molds, dies and high-temperature parts where high strength, good wear and oxidation resistance are required [5–14].

Mechanical alloying is an important non-equilibrium process and also one of the promising methods to produce nanocrystalline materials [15, 16]. The present work is the first attempt to consolidate the nanocrystalline equiatomic HEAs. In this work, the nanocrystalline equiatomic AlFeTiCrZnCu HEA have been synthesised by mechanical alloying and an attempt made to study the consolidation behaviour of the same with various routes. The elements of the HEA are carefully selected such that the size factor is low so that they easily form a solid solution with crystalline structure [4]. The microstructure and mechanical properties like hardness, compressive strength and wear resistance of the HEA were also studied. For wear studies nickel hard faced alloy is used as disc and AlFeTiCrZnCu HEA is used as a pin. The nickel-based hard facing alloys have become increasingly popular in recent years owing to their excellent performance under conditions of abrasion, corrosion and elevated temperature [17].

Experimental details

The nanocrystalline equiatomic AlFeTiCrZnCu HEA powders were prepared by high-energy ball milling by

S. Varalakshmi · M. Kamaraj · B. S. Murty (✉)
Department of Metallurgical and Materials Engineering, Indian Institute of Technology Madras, Chennai 600036, India
e-mail: murty@iitm.ac.in

G. Appa Rao
Defence Metallurgical Research Laboratory (DMRL), Hyderabad 500058, India

following the same procedure as described in our earlier study [4]. After the successful synthesis of nanocrystalline equiatomic AlFeTiCrZnCu HEA, the powders were consolidated by cold pressing and sintering, vacuum hot pressing (VHP) and hot isostatic pressing (HIP) in order to confirm the stability of structure and identify the suitable consolidation technique. The nanocrystalline equiatomic AlFeTiCrZnCu HEA was compacted with 2 GPa normal load at room temperature using a uniaxial press of 1000 ton capacity and heat treated at 800 °C for 1 h in argon atmosphere. The VHP was carried out with a semi-automatic, computer-controlled 250 ton load capacity press using graphite die with 65 mm diameter. The VHP was carried out at 800 °C with 30 MPa for half an hour. To avoid graphite diffusion, the wall of the die was coated with boron nitride and 1 mm of metal was removed from both surfaces of the VHP sample before its characterization. In the case of HIP, stainless steel cans with dimensions of 50 × 40 mm were prepared by welding the stainless steel sheets. The HIP was performed at 800 °C with 1 GPa pressure for half an hour. An EDM wire cutting was used for machining and cutting the VHP and HIP samples to the appropriate specifications to carry out the necessary characterization and mechanical property evaluation.

The sectioned samples were characterized by the X-ray diffraction technique (XRD) using a Brucker D8 X-ray diffractometer with Cu K_α radiation. The Netzsch STA409 PC DSC/TGA apparatus has been used to study the stability of the alloy at a constant heating rate of 20 K/min. The energy dispersive X-ray (EDX) microanalysis equipped with FEI-Quanta 200 scanning electron microscope (SEM) was used for compositional analysis and microstructure analysis. The sectioned and polished samples were used to measure the bulk hardness by Vickers hardness tester with 3 kg load and the compressive strength by 1000 kN press. The wear behaviour of the HIP sample was estimated using a pin-on-disc wear tester. For wear studies the nickel hard faced alloy was used as a disc and the AlFeTiCrZnCu HEA was used as a pin. In the present study 2-mm-thick austenitic stainless steel of type 316 LN was surfaced with a nickel-base hard facing alloy corresponding to AWS NiCr-B and was taken as a disc material. The deposition was made using plasma transferred arc (PTA) surfacing and the deposit consists of the precipitates like $(Ni,Fe)_3B$, Ni_3Si, Cr_7C_3, Cr_5B_3 and Cr_7B_3. The microhardness values are about 2000 VHN for the floret-like precipitates and about 1300 VHN for the needle-shaped particles in the hard face alloy. The average hardness of the deposit is around 550 VHN, which is maintained down to a distance of 0.5 mm from the interface. This available material is thought to be potential alloy to be used as a disc in the wear test [17]. The weight loss of the pin and disk after wear test were measured in order to estimate the wear loss. The wear debris and worn surfaces were characterized using SEM after the wear test.

Results and discussion

XRD and DSC analysis as nanocrystalline AlFeTiCrZnCu HEA

The XRD patterns of nanocrystalline equiatomic AlFeTiCrZnCu HEA are shown in Fig. 1, which evidences the phases formed in as milled and consolidated conditions, i.e. after 20 h of milling, cold press and heat treatment, VHP and HIP conditions. The XRD pattern shows the single BCC phase and small traces of WC impurity in the 20 h milled sample. This WC is a contamination from the milling media. The consolidated samples show the two BCC phases and a small volume fraction of FCC phase. The *d*-spacing calculations from the 2θ positions of the peaks present in the XRD pattern confirm these structures (Table 1). The DSC results shown in Fig. 2 clearly reveal that there is no predominant endothermic or exothermic peak up to 800 °C, which indicates that there is no phase change in the nanocrystalline equiatomic AlFeTiCrZnCu HEA up to 800 °C for 1 h. This suggests that the second BCC phase and the small fraction of FCC phase observed in the consolidated samples possibly existed in the as-milled condition itself. However, the small volume fraction of FCC phase is not visible in the as-milled condition due to the peak broadening caused by nanocrystalline nature of the FCC phase. Moreover, the very close lattice parameters of

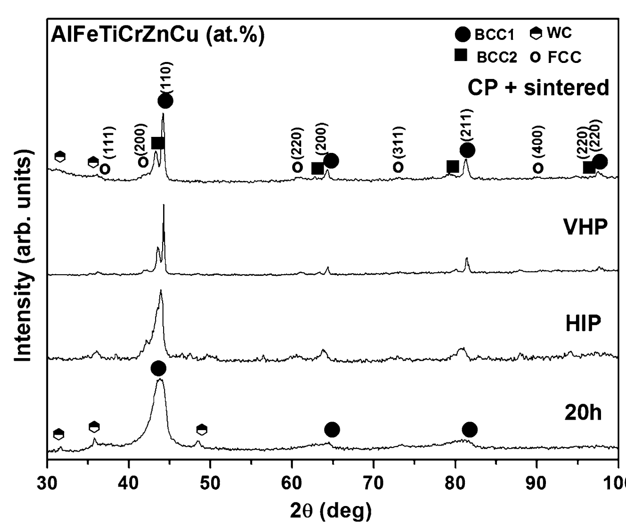


Fig. 1 XRD patterns of nanocrystalline equiatomic AlFeTiCrZnCu HEA with various consolidation routes (20 h: 20 h ball milled, *CP* cold pressed and sintered, *VHP* vacuum hot pressed, *HIP* hot isostatic pressed)

Table 1 Calculated and experimental *d*-spacing values of the phases present in nanocrystalline equiatomic AlFeTiCrZnCu HEA in heat treated condition

S. no.	Angle (2θ) (°)	*d*-spacing (experimental) (nm)	*d*-spacing (calculated) (nm)	Planes–crystal structure
1.	36.14	0.248	0.248	(111)–FCC
2.	42.30	0.214	0.215	(200)–FCC
3.	43.29	0.209	0.209	(110)–BCC1
4.	44.14	0.205	0.205	(110)–BCC2
5.	60.91	0.152	0.152	(220)–FCC
6.	62.83	0.148	0.148	(200)–BCC1
7.	64.31	0.145	0.145	(200)–BCC2
8.	72.96	0.130	0.130	(311)–FCC
9.	77.03	0.124	0.124	(222)–FCC
10.	79.41	0.121	0.121	(211)–BCC1
11.	81.28	0.118	0.118	(211)–BCC2
12.	89.92	0.109	0.108	(400)–FCC
13.	94.68	0.105	0.104	(220)–BCC1
14.	97.57	0.102	0.103	(220)–BCC2

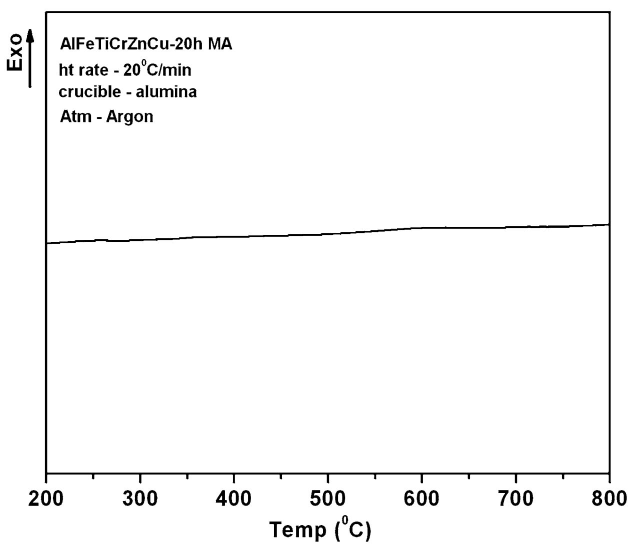


Fig. 2 DSC trace of 20 h milled nanocrystalline equiatomic AlFeTiCrZnCu HEA heated to 800 °C

the two BCC phases and peak broadening caused by nanocrystalline nature of the phases is the reason for the overlapping of the peaks in the as-milled condition.

Microstructure analysis of nanocrystalline AlFeTiCrZnCu HEA

The SEM analysis of the cold pressed and sintered sample (Fig. 3a) evidenced the more number of porosity, which is expected. As MA powders are prone to minimum plastic deformation during cold consolidation as they are already deformed extensively during the milling process. This study suggests that the simultaneous application of pressure and temperature might give better density in this alloy. In order to reduce the porosity and also retain the nanocrystalline nature with better mechanical properties, they have been consolidated using VHP and HIP.

The SEM-BSE micrograph shown in Fig. 3b proved that the nanocrystalline HEA can be processed using VHP with very little porosity. The SEM-BSE-EDX results are given in Table 2, which gives the compositions of the each phase present in the alloy. Phase 1, (light grey in Fig. 3b), labelled as grey-1, has all the six elements and is rich in Cu, Zn and Ti. Phase 2 (dark grey in Fig. 3b) labelled as grey-2 is rich in Al, Fe and Cr and depleted in Cu, Zn and Ti. Phase 3 (white in Fig. 3b) labelled as white is rich in Cu and Zn. From the volume fractions of the phases, it appears that the two grey (light and dark) coloured phases are the BCC phases and the white one is the FCC phase. The three-phase microstructure has also been confirmed in the HIPed sample by SEM–BSE image as shown in Fig. 3c. Table 2 gives the composition of each phase present in the alloy, which indicates the composition of the three phases in the HIPed alloy is similar to that of the three phases observed in VHP alloy. The XRD results are also similar in both the VHP and HIP samples. However, the microstructure and the distribution of the phases are different in HIPed sample in comparison to VHP sample. In the microstructure of the HIPed sample, the phases are spherical in shape and small in size, which is attributed to the isostatic pressure during the HIP process. According to the Gibb's phase rule ($F = C - P + 1$; F is the degree of freedom; C the number of components; P the number of phases), the maximum number of equilibrium phases in a C component system at constant pressure is $P = C + 1$. The value of P may even be greater under non-equilibrium conditions. The study of conventional alloys also indicates that a large number of intermetallic compounds or other complex

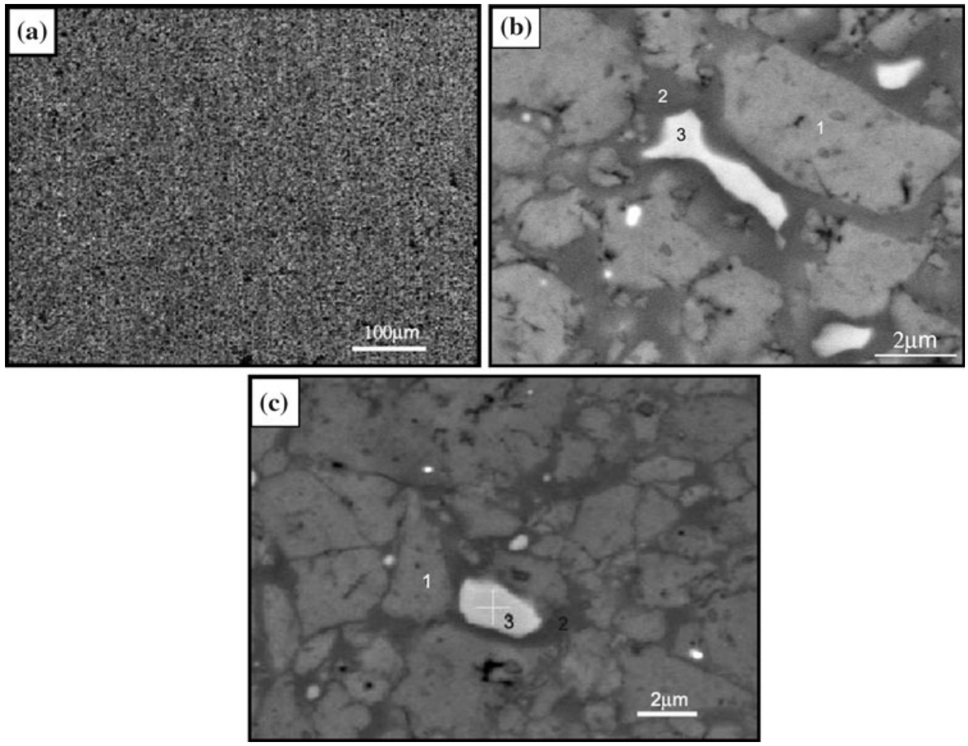


Fig. 3 SEM–BSE images of nanocrystalline equiatomic AlFeTiCrZnCu HEA: **a** cold pressed and sintered, **b** VHP and **c** HIP

Table 2 SEM-EDX results of nanostructured equiatomic AlFeTiCrZnCu HEA

Condition	Phase	Al (at.%)	Fe (at.%)	Ti (at.%)	Cr (at.%)	Zn (at.%)	Cu (at.%)
VHP	Bulk	18.0	16.1	16.4	16.8	16.2	16.5
	Grey-1	11.4	7.2	25.0	7.2	24.7	24.4
	Grey-2	27.6	31.6	4.1	30.1	3.0	3.5
	White	13.9	11.3	2.4	11.8	30.6	30.1
HIP	Bulk	18.9	16.2	15.7	15.9	17.2	16.1
	Grey-1	14.3	11.4	18.7	11.5	23.0	21.1
	Grey-2	24.9	28.7	5.3	28.4	6.2	6.5
	White	9.3	4.4	1.6	4.2	40.3	40.1

ordered phases are expected to form in multicomponent alloy systems. However, the total number of phases observed in nanocrystalline equiatomic AlFeTiCrZnCu HEA is well below the number of phases allowed by Gibb's phase rule. The phases present in the AlFeTiCrZnCu HEA are found to be stable up to 800 °C for 1 h.

The entropy of fusion of all the individual elements in the present system is less than that of configurational entropy of the hexanary system (14.9 J/mol K), which means the randomness due to the number of elements present in the system is higher than randomness caused by melting. This high configurational entropy (high randomness in the system) and also the large quantity of defects induced during MA may lead to the formation of simple crystal structure in this HEA. The formation of amorphous phase at the equiatomic composition in the present system is not observed, possibly due to the smaller differences in atomic sizes. The formation Cu–Zn, Al–Fe–Cr and Ti–Cu–Zn based solid solutions in the VHP and HIP alloy, instead of the formation of intermetallics, indicates the role of configurational entropy even after the alloy is heated to 800 °C.

Mechanical properties of AlFeTiCrZnCu HEA

The Vickers's bulk hardness of VHPed nanocrystalline equiatomic AlFeTiCrZnCu HEA is 9.50 GPa and the compressive strength is 2.19 GPa against fracture. The high values of hardness and strength might be attributed to the presence of a larger volume fraction of nanocrystalline BCC phases and minor FCC phase. The larger grain boundary area and the presence of three phase boundaries may be another reason for the higher strength of this alloy. The hardness and compressive strength of the HIPed nanocrystalline equiatomic AlFeTiCrZnCu HEA are 10.04 and 2.83 GPa, respectively, and are similar to those observed in the VHPed HEA.

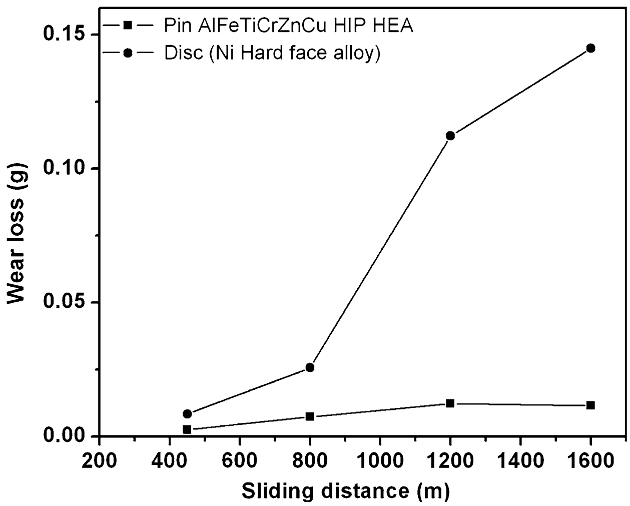
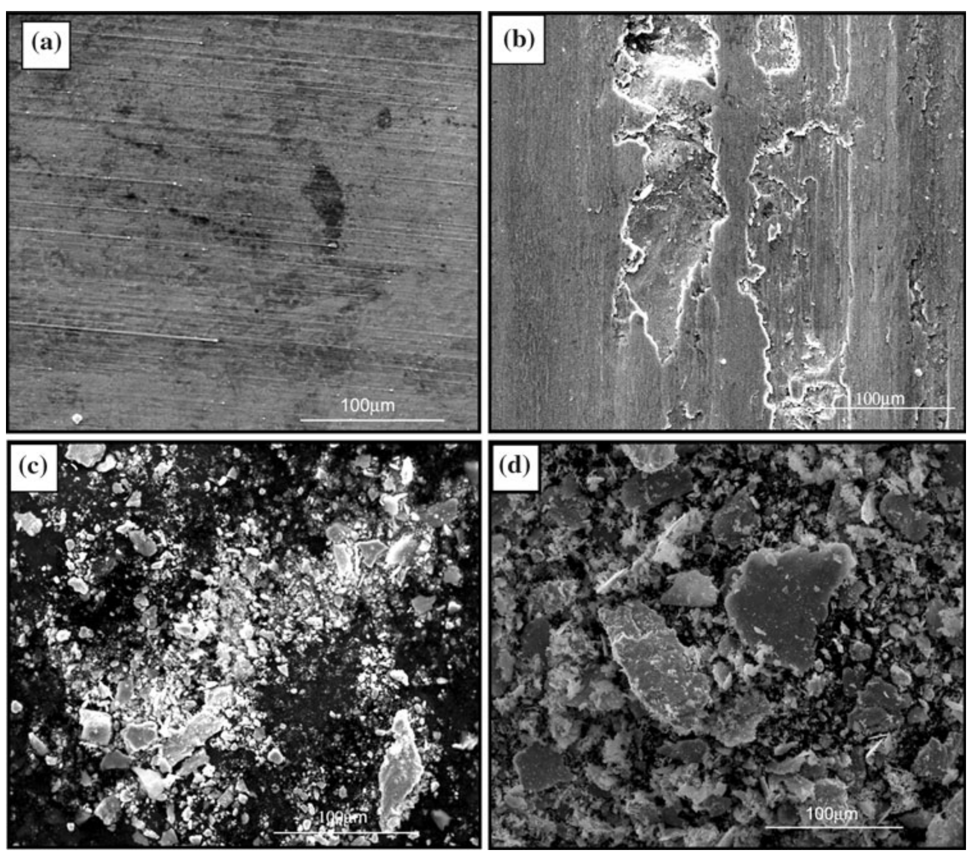


Fig. 4 Variation of wear loss with sliding distance

In general, nanocrystalline structure is expected to enhance the hardness and wear resistance of the material. Therefore, the present study on mechanical properties has been extended to evaluate the wear resistance of the HIPed AlFeTiCrZnCu HEA. A room temperature wear study was carried out using a pin-on-disc machine. A pin prepared from the HIPed AlFeTiCrZnCu HEA was used against the Ni-hard faced disc (hardness = 650 HV) at a constant load of 3 kg by varying track distance as 450, 800, 1200, and 1600 m. The results of the wear test are presented in Figs. 4 and 5. Figure 4 shows that the wear loss increases with sliding distance. However, the wear loss of HEA is significantly lower than the disc material. This clearly indicates that the HEA has better wear resistance than the Ni-hard faced alloy. The entropy of fusion of all the elements in the present system is less than that of the configurational entropy of the hexanary system (14.9 J/mol K), which means the randomness due to the number of elements present in the system is higher than the randomness in the melting. This high configurational entropy (high randomness in the system) and also the large quantity of defects induced during MA may lead to the formation of simple crystal structure in this HEA. The formation of amorphous phase at the equiatomic composition in the present system is not observed, possibly due to the smaller differences in the atomic sizes.

Fig. 5 SEM images of the wear tested pin at a sliding distance of **a** 450 and **b** 1600 m and those of wear debris (**c**) at a sliding distance of 450 and **d** 1600 m



This result was further supported by the SEM micrographs taken on worn surfaces (Fig. 5). Morphology of wear tracks on pin at varying sliding distance is given in Fig. 5a and b and accumulated debris at different sliding distance is shown in Fig. 5c and d. Figure 5a and b reveals that the formation of wear tracks on pin (HEA) is observed only at a sliding of 1600 m. No severe ploughing was observed at a lower sliding distance below 1600 m except some sort of macroscopic plastic deformation. These deformation marks were prominent with the increase in the sliding distance. When the sliding distance was increased to 1600 m, the surface of the pin showed severe ploughing, grooves and pullout due to the strong surface deformation as consequences of adhesive wear. Importantly, the wear did not induce any fracture or cracks on the HEA surface. Thus, the present results clearly reveal that wear on HEA was mainly due to the notable surface deformation and not by fracture. Based on these observations, it may be stated that the nanostructured HEA can be a good candidate for wear resistance applications.

Conclusions

The following conclusions can be drawn from the present investigations involving consolidation and mechanical properties of nanocrystalline AlFeTiCrZnCu HEA:

1. The nanocrystalline equiatomic AlFeTiCrZnCu HEA synthesized by MA has been studied with different consolidation processes and HIP is found to be the best in terms of densification and the mechanical properties.
2. The hardness and compressive strength of the nanocrystalline equiatomic AlFeTiCrZnCu HEA after VHP is 9.50 and 2.19 GPa and those after HIP are 10.04 and 2.83 GPa, respectively.
3. The wear resistance is found to be higher than the commercially used materials such as Ni-hard faced alloy.

References

1. Ranganathan S (2003) Curr Sci 85:1404
2. Yeh JW, Chen SK, Lin SJ, Gan JY, Chin TS, Shun TT, Tsau CH, Chang SY (2004) Adv Eng Mater 6:299
3. Yeh JW, Chen SK, Gan JY, Lin SJ, Chin TS, Shun TT, Tsau CH, Chang SY (2004) Metall Mater Trans A 35A:2533
4. Varalakshmi S, Kamaraj M, Murty BS (2008) J Alloys Compd 460:253
5. Cantor B, Chang ITH, Knight P, Vincent AJB (2004) Mater Sci Eng A 375–377:213
6. Chang HW, Huang PK, Yeh JW, Davison A, Tsau CH, Yang CC (2008) Surf Coat Technol 202:3360
7. Chen TK, Shun TT, Yeh JW, Wong MS (2004) Surf Coat Technol 188–189:93
8. Huang PK, Yeh JW, Shun TT, Chen SK (2004) Adv Eng Mater 6:74
9. Huang YS, Chen L, Lui HW, Cai MH, Yeh JW (2007) Mater Sci Eng A 457:77
10. Lai CH, Lin SJ, Yeh JW, Chang SY (2006) Surf Coat Technol 201:3275
11. Lin CH, Duh JG, Yeh JW (2007) Surf Coat Technol 201:6304
12. Tsai MH, Lai CH, Yeh JW, Gan JY (2008) Appl Phys Lett 92:052109
13. Zhang Y, Zhou YJ, Lin JP, Chen GL, Liaw PK (2008) Adv Eng Mater 10:534
14. Zhou YJ, Zhang Y, Wang YL, Chen GL (2007) Appl Phys Lett 90:181904
15. Murty BS, Ranganathan S (1998) Int Mater Rev 43:101
16. Suryanarayana C (2001) Prog Mater Sci 46:1
17. Gurumoorthy K, Kamaraj M, Prasad Rao K, Sambasiva Rao A, Venugopal S (2007) Mater Sci Eng A 456:11