

## In Situ Synthesis of Nanocrystalline Intermetallic Compound Layer during Surface Mechanical Attrition Treatment of Zirconium

SUN Cai-yun<sup>1</sup>, XIE Ji-jia<sup>1</sup>, WU Xiao-lei<sup>1</sup>, HONG You-shi<sup>1</sup>, LIU Gang<sup>2</sup>, LU Jian<sup>3</sup>, LU Ke<sup>2</sup>

1. State Key Laboratory of Nonlinear Mechanics, Institute of Mechanics, Chinese Academy of Sciences, Beijing 100080, People's Republic of China

2. Shenyang National Laboratory for Materials Sciences, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, People's Republic of China

3. LASMIS, University of Technical of Troyes, 10000, Troyes, France

**Abstract:** The surface mechanical attrition treatment (SMAT) technique was developed to synthesize a **nanocrystalline** (NC) layer on the surface of metallic materials for upgrading their overall properties and performance. In this paper, by means of SMAT to a pure zirconium plate at the room temperature, repetitive multidirectional **peening** of steel shots (composition (wt%): 1C, 1.5Cr, base Fe) severely deformed the surface layer. A NC surface layer consisting of the **intermetallic** compound **FeCr** was fabricated on the surface of the zirconium. The **microstructure** characterization of the surface layer was performed by using X-ray diffraction analysis, optical microscopy, scanning and transmission electron microscopy observations. The NC surface layer was about 25  $\mu\text{m}$  thick and consisted of the intermetallic compound FeCr with an average grain size of  $25 \pm 10$  nm. The deformation-induced fast diffusion of Fe and Cr from the steel shots into **Zr** occurred during SMAT, leading to the formation of intermetallic compound. In addition, the NC surface layer exhibited an **ultrahigh nanohardness** of 10.2 GPa.

**Key words:** nanocrystalline, intermetallic compound, surface layer, deformation, diffusion

THE FABRICATION of the nanocrystalline (NC) surface layer on bulk metallic materials has been attracting rapidly increasing interest because exciting new mechanical and physical **properties** can be expected. A recently developed technique, the surface mechanical attrition treatment (SMAT) [1], has shown to be capable of generating the NC surface layer in various metals and alloys [2-5]. This kind of surface **nanocrystallization** is achieved through creating localized severe plastic deformation, leading to continuous grain refinement down to the nanometer from original coarse grains without changing the chemical composition of the material. Another advantage of surface nanocrystallization is the great enhancement of the diffusion kinetics of atoms. For example, it has been reported that the **nitriding** temperature of the NC Fe produced using SMAT can be reduced to 300 °C, which is at least 200 °C below the conventional nitriding temperature [6]. The **diffusivity** of Cr in the NC Fe is 7-9 orders of magnitude higher than that in Fe lattice and 4-5 orders of magnitude higher than that in the grain boundaries of  $\alpha$ -Fe [7]. Moreover, some experimentally documented phenomenon have exhibit that diffusion in mechanically synthesized NC materials is definitely recognized as the strongly enhanced diffusion, compared to that in coarse-grained **polycrystals** and NC materials fabricated by non-mechanical (more equilibrium than mechanical) methods [8,9]. In addition, unusual fast atom diffusion may occur during plastic deformation even at the room temperature due

to the presence of both deformation-induced **nonequilibrium** grain boundaries and the refined grains, as in the case of mechanically alloying [10], and as a result, the sequence of solid state reactions may occur, e.g., the formation of supersaturated solid solution, intermetallic compound, and amorphous phase. Therefore, a strategy may be realized to generate the NC surface layer with novel phase structures different from the metallic matrix via deformation-induced atom diffusion in situ occurred during plastic deformation.

The intermetallic compounds are often lighter, stronger, **stiffer**, and more corrosion-resistant than ordinary metals, particularly at high temperatures. Yet their uses are limited because they have persistent problems with low ductility and poor fracture toughness at room temperature, making them difficult to fabricate and vulnerable to fracture. These major drawbacks, however, could be substantially improved by processing materials with **nanostructures** [11]. Several methods **including** rapid self propagating synthesis reaction and thermal spraying may yield the nanostructures [12,13]. The resultant structures are, however, with residual porosity and contamination. These difficulties have been substantial roads-blocks to the structural applications of the intermetallic surface layer and coating. As a consequence of above limitations, the mechanical means based on severe plastic deformation is much likely to solve the problem by introduction of the intermetallic compounds **with** an in situ way.

In the present study, we synthesized for the first time

an NC surface layer with in situ formed intermetallic compounds on the bulk Zr by using the SMAT technique. The surface layer consisted of intermetallic compound FeCr with an average grain size  $25 \pm 10$  nm. The intermetallic phase was in situ formed via atom diffusion during plastic deformation. The surface layer also exhibited an **ultrahigh nanohardness** of 10.2 GPa.

## 1. Experimental Procedure

The material used in this study is the pure zirconium with the chemical composition (wt%), 0.15 Fe, 0.03 Cr, 0.007 Ni, 0.01 Hf,  $O < 0.16$ , 0.0065 N, base Zr. The specimen had a shape of  $5 \times 50 \times 100$  mm<sup>3</sup> in size. The specimen was vacuum annealed for 2 hours at 950°C.

During the SMAT process, the hardened steel balls of 8 mm in diameter (chemical composition (wt%): 1 C, 1.5 Cr, base Fe) were placed at the bottom of a cylinder-shaped vacuum chamber attached to a vibration generator, with which the balls were resonated. Because of the high vibration frequency of the system, the sample surface to be treated was peened repetitively by a large number of balls within a short period of time. Each peening of the ball to the surface resulted in localized plastic deformation in the surface layer of the treated sample. As a consequence the grains in the surface layer were expected to be effectively refined. A detailed description of the SMAT apparatus used in this study can be found elsewhere [1,2]. In the present work, the SMAT was performed under vacuum at room temperature for 50 minutes with a vibrating frequency of 50 Hz.

Following SMAT, the microstructure characterization of the surface layer was performed in an optical microscope, X-ray diffraction (XRD), scanning electron microscope (SEM) and transmission electron microscope (TEM). The hardness of the surface layer was also measured using a nanohardness indenter.

## 2. Experimental Results

Fig. 1 (a) shows the XRD pattern of the as-annealed Zr before SMAT. The Zr reveals a hexagonal close packed (hcp) structure. Note that the Miller indices corresponding to each peak have also indicated. Fig. 1 (b) is the XRD pattern of the treated top surface of Zr after SMAT. It is of special interest to note the formation of the intermetallic compound FeCr with a cubic structure. The widening of the diffraction peaks is also observed. This is due to the crystallite size refinement and the increase in microstrains associated with the severe deformation.

Fig. 2(a) is an optical image showing the cross-section of the SMATed sample. The deformation-affected zone has the depth of about

120  $\mu$ m, with a continuous grain refinement from inside towards the treated top surface. The grain boundary

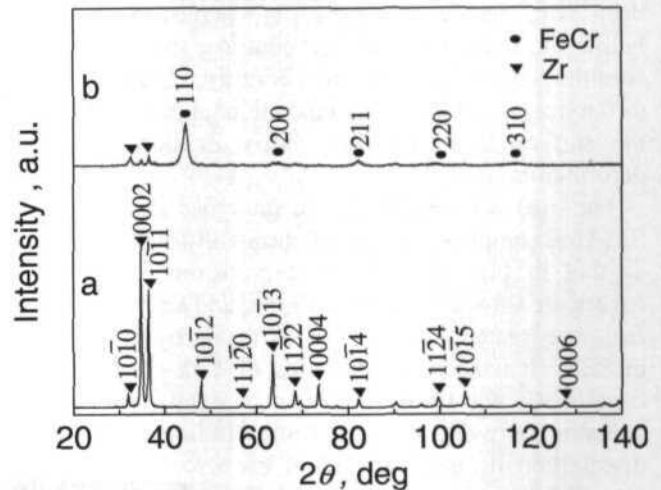


Fig. 1 XRD patterns of (a) as-annealed and (b) treated top surface after SMAT.

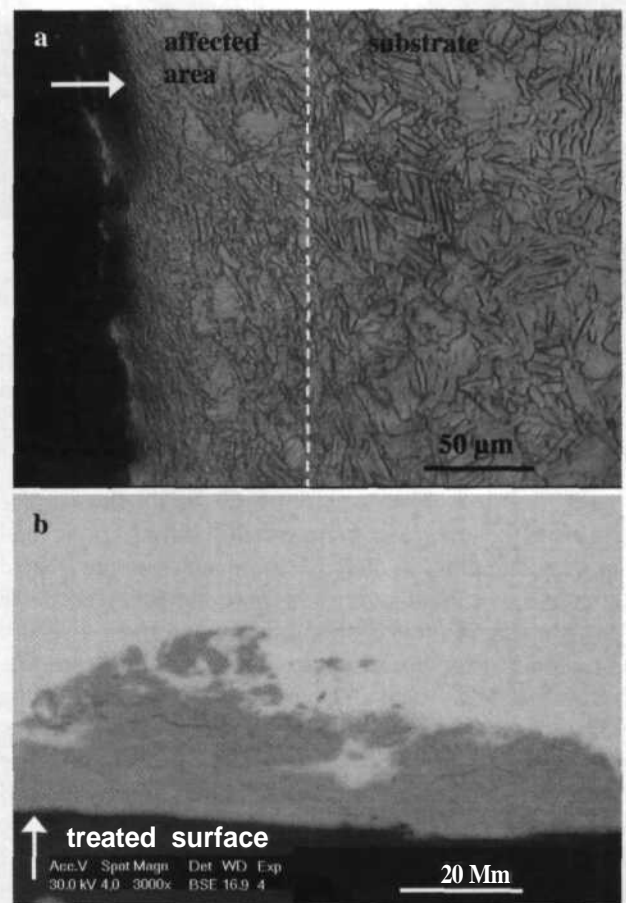


Fig. 2 Cross-section images of the SMATed sample. (a) Optical image and (b) BSE image by SEM. The arrowheads indicate the SMATed surface.

contrasts almost disappear much near the treated

surface. Fig. 2(b) is an unetched cross-section of the SMATed sample using backscatter electron (BSE) imaging in SEM. A thin surface layer of about 25  $\mu\text{m}$  deep with dark-grey contrast is visible, located just below the treated surface. In contrast, the inside area exhibits a uniform light-grey contrast. Therefore, the difference in chemical composition appears between the surface layer and the matrix Zr during plastic deformation.

Fig. 3(a) is a SEM image of the cross-section of the SMATed sample. The same contrast difference is seen as that in Fig. 2(b). Three composition distribution curves are shown relevant to Zr, Fe, and Cr respectively from the treated surface towards inside by using EDX in SEM. It is seen that the area of dark-grey contrast contains Fe and Cr whereas that of light-grey contrast contains only Zr. Figs. 3(b)-(d) indicate elemental distribution in an area marked by a rectangle in (a). Note the presence of Fe and Cr within the thin surface layer of dark-grey contrast. Therefore, it is concluded that Fe and Cr diffuse from steel balls into the surface of the Zr specimen during the SMAT process.

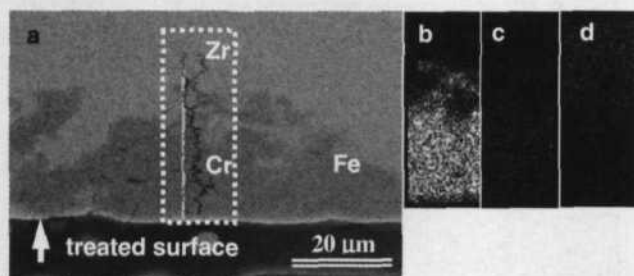


Fig.3 Chemical composition analysis by EDAX in SEM. (a) line-scanning curves relevant to Fe, Cr, and Zr respectively. (b)-(d) area-scanning of Fe, Cr, and Zr respectively.

Fig. 4(a) is a cross-sectional TEM bright-field image showing the interface between the surface layer and substrate at approximately 25  $\mu\text{m}$  deep from the treated top surface. It is of interest to note the presence of an abrupt change in the grain size at the interface. Fig. 4(b) is the microstructure of approximately 5  $\mu\text{m}$  deep. The NC grains are visible. The inset is the corresponding selected-area electron diffraction pattern (EDP). A set of rings indicated that the NC grains are the intermetallic compound FeCr of random orientations with a bcc crystal structure, well consistent with the XRD analysis in Fig. 1(b). Fig. 4(c) is the TEM bright-field image showing the microstructure of about 35  $\mu\text{m}$  deep from the treated surface. The equiaxed Zr grains are visible within the submicrometer size regime. The inset is the ring-like EDP showing the hcp structure of Zr.

According to a statistical analysis of TEM

micrographs, the grain size distribution is measured. Figs. 5(a) and (b) are the histograms showing the size distribution of both FeCr and Zr at about 5 and 35  $\mu\text{m}$  deep respectively. One may find that the grain sizes

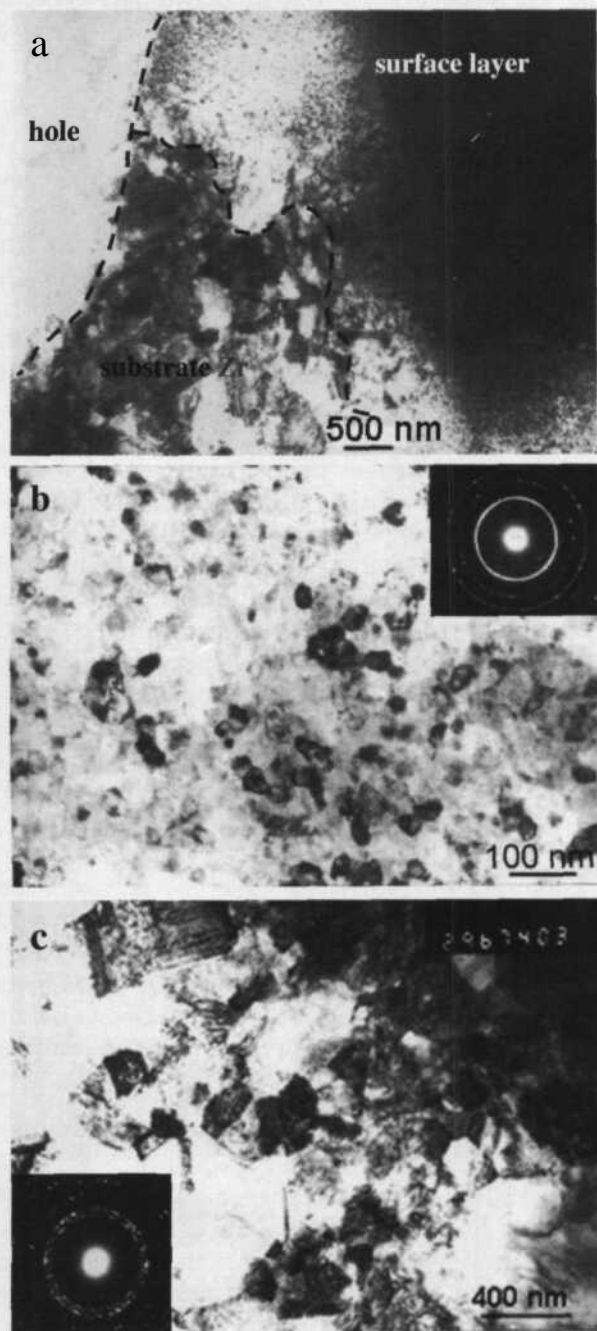


Fig. 4 TEM images showing (a) an abrupt change in grain size at the interface between the surface layer and the substrate at about 22  $\mu\text{m}$  deep, (b) nanograins of intermetallic compound FeCr at about 5  $\mu\text{m}$  deep. Inset is the corresponding EDP. (c) refined Zr grains of about 35  $\mu\text{m}$  deep from the treated surface. Inset is the corresponding EDP.

of FeCr range from 5 to 60 nm and have an average value of  $25 \pm 10$  nm. The Zr grains size have an average size of 280 nm, indicative of the significant grain refinement during SMAT.

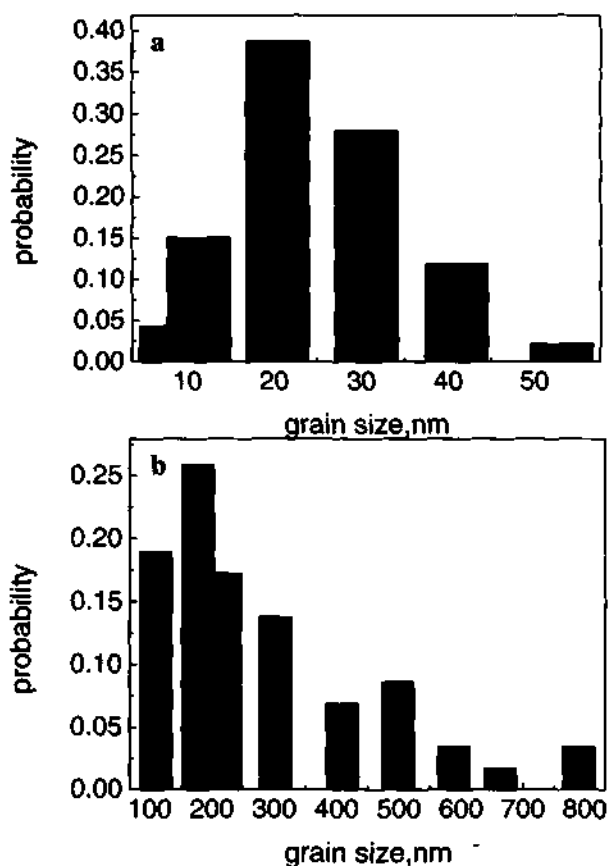


Fig. 5 Histograms showing grain size distribution of (a) FeCr and (b) Zr.

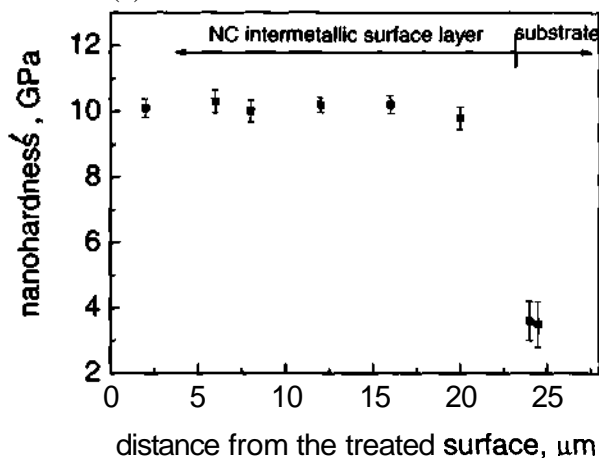


Fig. 6 The dependence of nanohardness on the depth of the surface layer.

The nanohardness of the SMATed sample is plotted in Fig. 6(a) as a function of the depth. The data indicate an average above 8 indents at a constant loading rate to a depth of 1  $\mu\text{m}$ . The nanohardness is around 10.2 GPa

within the surface layer consisting of intermetallic phase FeCr, much higher than 3.4 GPa in the adjacent area of pure Zr.

### 3. Discussion

During the SMAT process the high-energy steel balls peen repetitively the treated surface of the sample. Taking into consideration the high impact velocities and high impact frequencies of balls, direct and fast diffusion of Fe and Cr may occur from the steel balls into the treated surface of Zr, similar to the case happened in the process during mechanical alloying (MA) [10]. During MA, the formation of the wide spectrum of stable and unstable phases and compounds is possible due to strong mechanical action at relatively low temperatures (usually  $0.3-0.5 T_m$ ,  $T_m$  is the melting point, Kelvin) [10]. The idea of deformation-induced interdiffusion of components during MA gives a very simple explanation of results in our case. Meanwhile, the FeCr nanograins contain a considerable volume fraction of grain boundaries (GBs), which may serve as numerous fast diffusion "channels" [7,8]. Moreover, the GBs are in a high-energy non-equilibrium state. The energy stored in the non-equilibrium GBs may either facilitate diffusion along GBs for decreasing the defect formation energy or serve as a driving force for the formation of a solid solution [7,8,14]. The rapid diffusion of atoms from one grain into other leads to quick homogenization of Fe and Cr and continuous formation of FeCr intermetallic phase within the surface layer during SMAT. Another possible hypothesis for atom diffusion during SAMT could be the local temperature rise  $\Delta T$  that takes place during SMAT owing to the impacts between steel balls and specimen surface. Several reports gave estimations of  $\Delta T$  to be between 10 and 120 K during MA, depending upon the milling type [10]. As for Zr, however, this  $\Delta T$  is only  $0.15 T_m$ . As a result, the localized temperature rise is not likely contributes much to atom diffusion. One important question remains unsolved on the formation of intermetallic compound FeCr rather than FeZr and CrZr during SMAT. The solid reaction depends on the enthalpy between two elements [10]. It is much likely that the enthalpy between Fe and Cr is smaller than that between Fe and Zr and between Cr and Zr. A further detailed study of the mechanism of the intermetallic compounds is required.

The grain refinement is realized during the SMAT process as can be seen in Fig. 4(b). This is in line with other work devoted to SMAT [2-5] and can be well understood by grain subdivision mechanism in order to accommodate strains during deformation. With increasing strain, the dislocation boundaries of various patterns form and then separate the original coarse grains into cell blocks and subgrains. The

**misorientations** of dislocation boundaries increase with increasing strain and will become high angle boundaries with sufficient strain [2-4].

The **nanocrystallized intermetallic** layer also exhibits a high **nanohardness**, as can be seen in Fig. 5. This stems mainly from significant **reduction** of grain sizes down to the **nanoscale** range.

#### 4. Summary

A **nanocrystalline** surface layer consisting of **intermetallic** phase FeCr was in situ generated during the surface mechanical **attrition** treatment (**SMAT**) of Zr. Repetitive peening of steel balls (**wt%** chemical composition: 1C, 1.5 Cr, base Fe) results in introduction of Fe and Cr into the Zr by means of deformation-induced diffusion.

From the present work, the SMAT technique appears as being a well suitable one for the room temperature synthesis of the **intermetallic** surface layer in the bulk metallic materials. The SMAT technique has also proved itself to be superior to thermal spray methods for processing the **nanocrystalline** intermetallic coatings. The latter method often introduces various artifacts in the coating, such as contaminations, flaws and voids due to the imperfect **particulate** bonding **and/or** porosity induced in the processing procedures.

#### Acknowledgment

The research was supported by the National Natural Science Foundation of China and the Chinese Academy of Sciences.

#### References

- 1 Lu K and Lu J. Surface **nanocrystallization** (SNC) of metallic materials-presentation of the concept behind a new approach. J Mater Sci **Technol**, 1999,15:193-197.
- 2 Tao N R, Sui ML, Lu J and Lu K. Surface Nanocrystallization of Iron Induced by Ultrasonic Shot Peening. **Nanostru Mater**, 1999,11:433-440.
- 3 Liu G, Lu J, Lu, K. Surface nanocrystallization of 316L stainless steel induced by ultrasonic shot peening. Mater Sci Eng, 2000,A286: 91-95.
- 4 Wu X, Tao N, Hong Y, Xu B, Lu J, Lu K. **Microstructure** and evolution of mechanically-induced **ultrafine** grain in surface layer of **AL-alloy** subjected to **USSR Acta mater**,2002,50:2075-2084.
- 5 Tao NR, Wang ZB, Tong WP, Sui ML, LU J, Lu K. An investigation of surface nanocrystallization mechanism in Fe induced by surface mechanical attrition treatment. Acta mater 2002,50:4603-4616.
- 6 Tong WP, Tao NR, Wang ZB, Lu J, Lu K. **Nitriding** iron at lower temperatures. Science ,2003,299:686-8.
- 7 Wang ZB, Tao NR, Tang WP, Lu J, Lu K. Diffusion of chromium in nanocrystalline iron produced by means of surface mechanical attrition treatment. Acta mater, 2003,51:4319-4329.
- 8 Baro MD, Kolobov Yu-R, Ovid'ko IA, Schaefer H-E, Straumal BB, Valiev RZ, Alexandrov IV, Ivanov M, Reimann K, Reizis AB, Surinach S, Zhilyaev AP. Diffusion and related **phenomena** in bulk nanostructured materials. Rev Adv Mater Sci, 2001,2(1): 1-43.
- 9 Yu Gutkin M, Ovid'ko IA, Pande CS. Theoretical models of plastic deformation **processes** in nanocrystalline materials. Rev Adv Mater Sci, 2001,2(1): 80-102.
- 10 Suryanarayana C. Mechanical alloying and milling. Prog Mater Sci, 2001,46:1-184.
- 11 Koch CC, Morris DG, Lu K, Inoue A. Ductility of nanostructured materials. MRS Bulletin, 1999,24:54-58.
- 12 Hearley JA, Little JA, Sturgeon AJ. The effect of spray parameters on the properties of high velocity **oxy-fuel NiAl** intermetallic coatings. Surf Coat Technol, 2000,123:210-218.
- 13 Grosdidier T, Tidu A, Liao HL. **Nanocrystalline** Fe-40Al coating processed by thermal spraying of milled powder. Scr Mater, 2001,44:387-393.
- 14 Yermakov AYe, Gapontzev VL, Kondratyev VV, Gornostyrev YuN, Uimin MA, Korobeinikov AYU. Phase instability of nanocrystalline driven alloys. Mater Sci Forum, 2000,343-346:577-584.