PREPARATION OF NiAl-FeSi COMPOSITES BY POWDER METALLURGY

[1]Pavel NOVÁK, [1]Stanislav MESTEK, [1]Alena MICHALCOVÁ, [2]Kateřina SKOTNICOVÁ, [2]Ivo SZURMAN

[1]Department of Metals and Corrosion Engineering, University of Chemistry and Technology, Prague, Czech Republic, EU, panovak@vscht.cz

[2]Faculty of Materials Science and Technology, VSB-Technical University of Ostrava, Ostrava-Poruba, Czech Republic, EU

https://doi.org/10.37904/metal.2023.4662

Abstract

This work deals with the development of the preparation route for the composites with nickel aluminide reinforced by FeSi particles. The optimization of mechanical alloying of individual phases, mixing and consolidation by spark plasma sintering is presented. The composite is developed for the application as a future tool material. As the optimum conditions of mechanical alloying, the milling durations of 4 h and 10 h can be recommended for the synthesis of NiAl and FeSi phases, respectively. The hardness of composites increases with the amount of FeSi phase.

Keywords: Nickel aluminide, iron silicide, composite, mechanical alloying, spark plasma sintering

1. INTRODUCTION

European Commission launched the list of critical raw materials (CRM) in 2011 [1]. This activity promoted the research leading to the substitution or improved recycling of raw materials, which are of high economic importance and high supply risk simultaneously. This list is a subject of regular updates due to the changes in geopolitical situation and developments in industry. Among the tool materials, the current list contains W and Co, which are included in cemented carbides or in high-speed steels. So there is an effort to substitute these materials (or just the particular elements) by a reasonable alternative [2]. This substitution is moreover driven by the health aspects of the use of cobalt-containing materials [3]. In recent years we worked on the possible substitution of these materials by Ti-Al-Si alloys, which are in fact "in-situ" Ti_5Si_3 – TiAl or Ti_3Al composites [4]. The materials were prepared by various methods, including powder metallurgy processes and also directional solidification, which enabled to grow fiber-reinforced Ti_5Si_3 – Ti_3Al composites [5]. However, the feasibility of this substitution is limited by low fracture toughness of Ti-Al-Si materials, anisotropy of the thermal expansion coefficient of Ti_5Si_3 phase [6] and also by the fact that titanium was newly listed as a critical raw material in 2020 [1]. There were also other researches dealing with intermetallic composites running, such as aluminide - ceramics [7-9] or silicide – ceramics [10,11] or silicide-aluminide coatings [12-14].

This work deals with the preparation of a potential CRM-free (or low-CRM) tool material – a NiAl-FeSi composite, where nickel aluminide forms the matrix, while iron silicide, being the hard phase, acts as the reinforcement. In this paper, the development of the preparation route by the combination of mechanical alloying and spark plasma sintering is described.

2. MATERIALS AND METHODS

The NiAl-FeSi composite with the weight ratio of aluminide to silicide 1:1 was prepared by separate synthesis of nickel aluminide and iron silicide by mechanical alloying. The mixtures of the chemical composition corresponding to NiAl and FeSi were prepared from elemental pure powders, which were mixed in appropriate amounts forming 20 g powder batches for mechanical alloying (MA). The following powders were used to prepare the blend for MA: Fe (purity 99.9 %, particle size <44 μm, Strem Chemicals), Al (purity 99,7 %, particle size <44 μm, Strem Chemicals), Si (purity 99.5 %, particle size <44 μm, Alfa Aesar) and Ni (purity 99.99 %, particle size <150 μm, Strem Chemicals). Mechanical alloying of the blends was carried out in a planetary ball mill Retsch PM100, where the milling jar and also milling balls were made of AISI 420 stainless steel. Argon was used as the protective atmosphere during mechanical alloying. The mechanical alloying conditions were following: duration of 2 – 10 h, change of rotation direction each 15 min, rotational velocity of 400 rpm, batch of 20 g and the ball-to-powder weight ratio of approx. 15:1.

Mechanically alloyed powders were consolidated to cylindrical samples of 20 mm in diameter by spark plasma sintering (SPS, FCT Systeme HP-D10, Rauenstein, Germany) at the temperature 1000 °C with a pressure of 48 MPa for 10 min. The heating rate of 300 °C/min was used in this process, while the samples were cooled by the rate of 50 °C/min after the sintering process was completed.

The phase composition of the mechanically alloyed powders, consolidated and annealed samples were examined by X-ray diffraction (XRD) analysis (X’Pert Pro diffractometer) using CoK radiation.

Microstructure of the materials in the state of mechanically alloyed powders and consolidated samples was observed using Nikon MA200 optical microscope after etching by modified Kroll’s reagent (10 ml HNO_3, 5 ml HF, 85 ml H_2O). TESCAN VEGA 3 LMU scanning electron microscope equipped by an energy-dispersive spectrometer X-max 20 mm^2 (EDS, Oxford Instruments, High Wycombe, United Kingdom) was used for local analysis of elemental composition.

3. RESULTS

Phase composition of the Ni-Al powders, determined by XRD, after various mechanical alloying durations is shown in **Figure 1**. It can be seen that nickel aluminide is present already after 2 h of mechanical alloying, but it is still accompanied by nickel. Unreacted nickel disappears after 4 h of the mechanical alloying process. After milling for 6 – 10 h, Ni_3Al_4 phase appears in the powders.

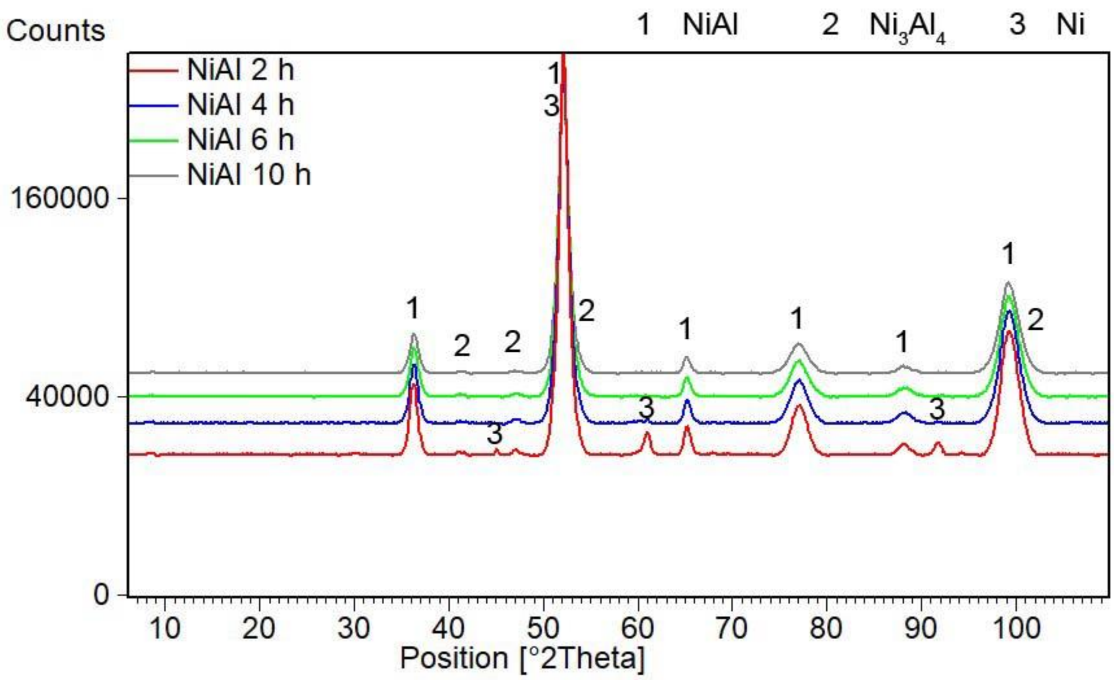

Figure 1 X-ray diffraction patterns of the mechanically alloyed Ni-Al powders vs. milling duration

The observation of microstructure after mechanical alloying revealed the presence of light particles, whose amount increased with growing milling duration (see **Figure 2**). These particles were rich in iron and chromium (up to 12.5 wt.% of Cr, as identified by EDS), which results from the milling balls and walls of the milling vessel, as a result of the wear of the equipment. Based on the facts presented above, the optimal duration of mechanical alloying process was determined as 4 h for nickel aluminide.

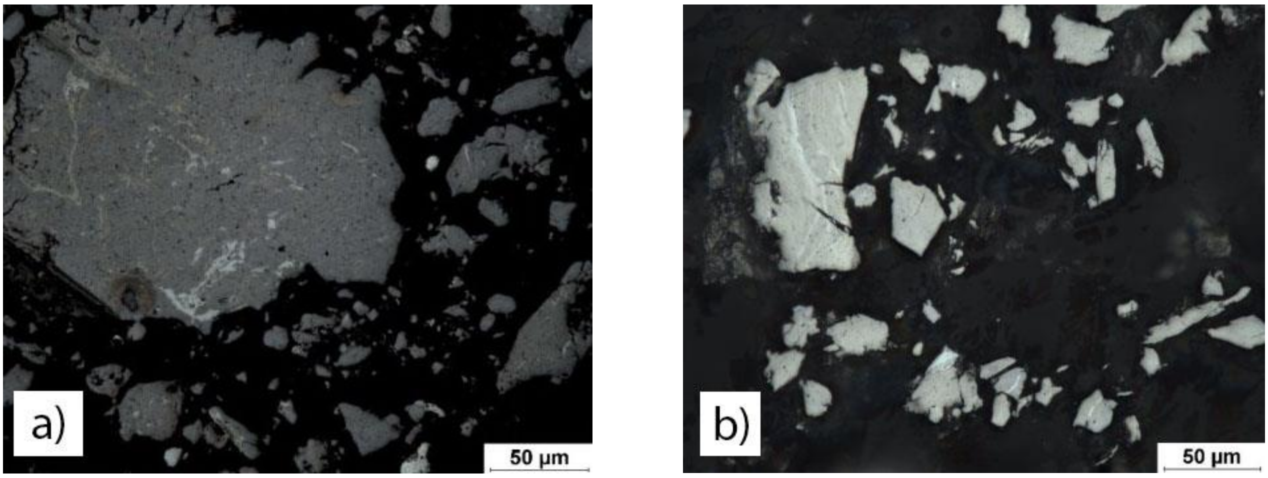

Figure 2 Optical micrographs of mechanically alloyed Ni-Al powder after milling for a) 2 h, b) 10 h

In the case of mechanical alloying of Fe-Si powders, FeSi phase appeared also already after 2 h of milling, but up to 6 h it was accompanied by unreacted iron and silicon. These phases were not present after 10 h of milling, and the final product contained also Fe_3Si and $FeSi_2$ phases in minor amounts (see **Figure 3**). The microstructure observation showed the lamelar structure, containing light lamellae of iron after 2 h of milling and visible homogenization of the material and refinement of the particles with increasing process duration (**Figure 4**). Based on the phase composition, the mechanical alloying for 10 h was determined as the optimal way for the preparation of Fe-Si phase.

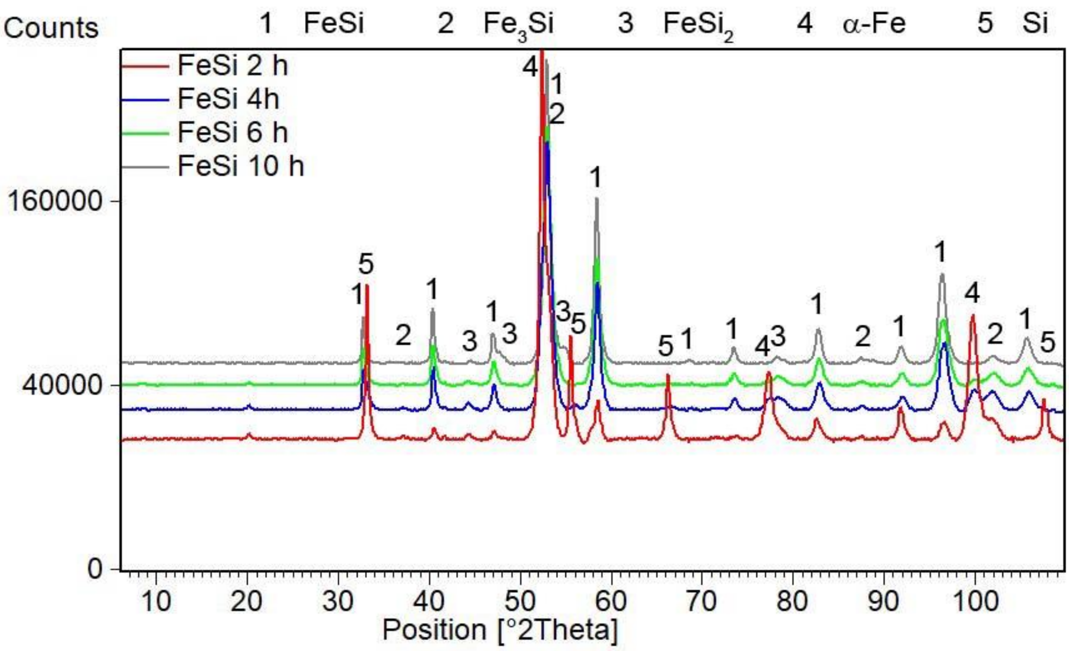

Figure 3 X-ray diffraction patterns of the mechanically alloyed Fe-Si powders vs. milling duration

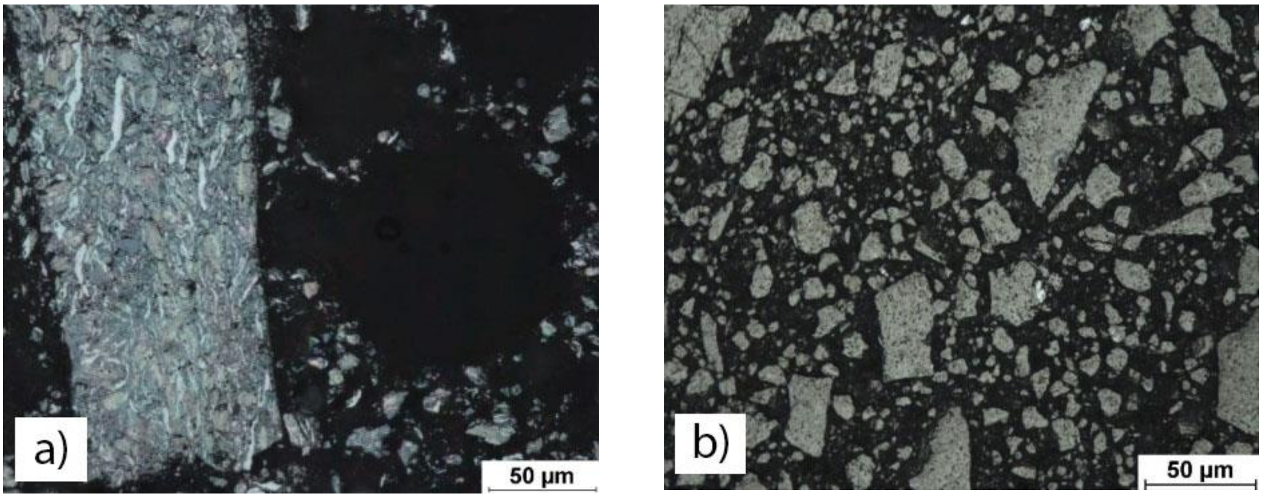

Figure 4 Optical micrographs of mechanically alloyed Fe-Si powder after milling for a) 2 h, b) 10 h

The powders obtained by optimized mechanical alloying, i.e. milling 4 h for NiAl and 10 h for FeSi, were blended in 1:1 weight ratio and sintered by the spark plasma sintering method. The resulting structure is shown in **Figure 5**. There are regions of light phase, which is the nickel aluminide, and darker ones being based on iron silicide. The determination of the properties of the composite will be the subject of further work.

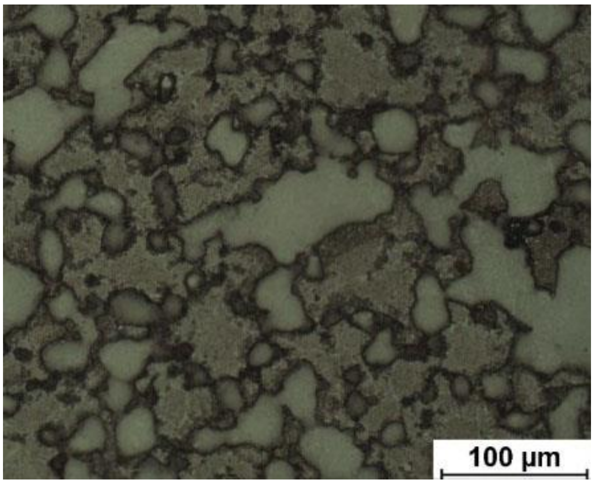

Figure 5 Optical micrograph of FeSi-NiAl composite after spark plasma sintering at 1000 °C for 10 min

4. DISCUSSION

Mechanical alloying is usually presented as the technology, which can bring even the materials, which cannot be obtained by conventional processing methods, e.g. alloys non-miscible elements, such as Mg-Fe [15,16]. Moreover, the powders are severely plastically deformed during the mechanical alloying process, leading to ultrafine-grained materials with improved mechanical properties. On the other hand, common mechanical alloying process usually takes 20 – 100 hours [17]. In our case, the mechanical alloying process was optimized based on our previous works [4], so that the intermetallics can be obtained in much shorter time. The optimization included the adjustment of the ball-to-powder ratio, batch and rotational velocity in order to bring maximal energy to the batch. The result is a process with high ball-to-powder ratio of 10:1 to 30:1, batch of 20 g in 500 ml vessel and rotational velocity of 400 rpm. It led to obtaining the almost pure

NiAl powder in 4 h, but FeSi powder after 10 h and still containing also other silicides ($FeSi_2$ and Fe_3Si). The reason for this difference probably lies in different mechanism of the mechanical alloying process. In preparation of NiAl phase, there are two ductile initial components. In such a case, lamellar structure usually forms very quickly. It leads to shorter diffusion paths between the reacting components and therefore, the mutual reaction can proceed quite quickly. In our optimized mechanical alloying process, the friction is also employed significantly, as no lubricant is used. The heat dissipated from the friction energy can be used for initiation of mutual reactions between nickel and aluminium, which are exothermic, but thermally activated. The temperature needed for the activation is close to the melting point of aluminium [18].

In the case of the silicide, the situation is different. Silicon behaves as brittle during the milling procedure. Therefore, it is fractured during the milling, and becomes incorporated in iron powder, which behaves plastically. The particles of incorporated silicon can also form bands that look like a lamellar structure (**Figure 4a**). What is the major difference from the formation of aluminide phase is higher initiation temperature silicide forming reaction [19]. Due to these facts, longer mechanical alloying process is needed to ensure sufficient fracturing of silicon to small particles and also to generate sufficient heat in order to initiate the silicide-forming reaction in the milling vessel.

The fact that nearly pure NiAl nickel aluminide was produced, while there was a mixture of FeSi, $FeSi_2$ and Fe_3Si in the case of iron silicide, can be probably explained on the basis of equilibrium phase diagrams of these systems [20]. While the NiAl phase has a wide range of stability in the Ni-Al phase diagram, the range of stability of FeSi phase is close to the line with exact chemical composition. Therefore the silicide tends to coexist with its neighbours (Fe_3Si and $FeSi_2$) in the phase diagram.

The resulting product after sintering contains the same phases as the mechanically alloyed powder. It implies that no reaction proceeds between nickel aluminide and iron silicide in the given temperature interval. The next step surely has to be the optimization of the NiAl : FeSi ratio, based on the characterization of the properties of the sintered materials.

5. CONCLUSION

This work was focused on the synthesis of composite, composed of FeSi and NiAl phases. These constituents were synthesized by mechanical alloying separately and then blended and sintered. For the mechanical alloying synthesis of NiAl phase, the duration of 4 h was determined as the optimum, while for FeSi a longer process of 10 h can be recommended. The composite was successfully sintered by spark plasma sintering method at the temperature of 1000 °C for 10 min. This work will be followed by detailed characterization of the composite and manufacturing of composites with varying ratio of FeSi and NiAl phases.

ACKNOWLEDGEMENTS

This research was financially supported by Czech Science Foundation, project No. 23-05126S. The authors would like to thank David Nečas for sintering of the sample.

REFERENCES

[1] Critical raw materials. *European Commission*. [online]. Available from: https://single-market-economy.ec.europa.eu/sectors/raw-materials/areas-specific-interest/critical-raw-materials_en.

[2] RIZZO, A., GOEL, S., GRILLI, M. L., IGLESIAS, R., JAWORSKA, L., LAPKOVSKIS, V., NOVAK, P., POSTOLNYI, B.O., VALERINI, D. The critical raw materials in cutting tools for machining applications: A Review. *Materials.* 2020, vol. 13, p. 1377.

[3] Cobalt and you. Working with cobalt – are you risk? *Health and Safety Executive*. [online]. Available from: https://www.hse.gov.uk/pubns/indg442.pdf

[4] KNAISLOVÁ, A., NOVÁK, P., CABIBBO, M., JAWORSKA, L., VOJTĚCH, D. Development of TiAl-Si Alloys – A Review. *Materials.* 2021, vol. 14, p. 1030.

[5] VOJTĚCH, D., NOVÁK, M., NOVÁK, P., LEJČEK, P., KOPEČEK, J. Unidirectional crystallization and high-temperature oxidation of in situ $Ti_3(Al,Si)$-$Ti_5(Si,Al)_3$ composite. *Materials Science and Engineering A.* 2008, vol. 489, pp. 1-10.

[6] SCHNEIBEL, H., RAWN, C.J. Thermal expansion anisotropy of ternary titanium silicides based on Ti_5Si_3. *Acta Materialia.* 2004, vol. 52, pp. 3843-3848.

[7] AZARMI, F. Creep properties of nickel aluminide composite materials reinforced with SiC particulates. *Composites Part B: Engineering.* 2011, vol. 42, pp. 1779-1785.

[8] YANG, J.-M., KAO, W.H., LIU, C.T. Development of nickel aluminide matrix composites. *Materials Science and Engineering A.*1989, vol. 107, pp. 81-91.

[9] MACKAY, R.A., BRINDLEY, P.K., FROES, F.H. Continuous fiber-reinforced titanium aluminide composites. *JOM.* 1991, vol. 43, pp. 23–29.

[10] YEH, C.-L., CHEN, K.-T., SHIEH, T.-H. Effects of Fe/Si stoichiometry on formation of Fe_3Si/FeSi-Al_2O_3 composites by aluminothermic combustion synthesis. *Metals*. 2021, vol. 11, no. 11, p. 1709.

[11] SCHOLL, R., TSAKIROPOULOS, P., BÖHM, A., KIEBACK, B. Properties of silicides and silicide composites densified by pressureless reactive sintering. *Materials Science Forum.* 1998, vol. 299–300, pp. 165–170.

[12] ZHANG, P., GUO, X. Preparation and oxidation resistance of silicide/aluminide composite coatings on an Nb–Ti–Si based alloy. *Surface and Coatings Technology*. 2015, vol. 274, pp. 18-25.

[13] KOCHMANSKA, A.E., JARLACZYNSKA, A., BARANOWSKA, J. Formation of silicide and silicide-aluminide coatings on molybdenum alloy during slurry cementation process: Influence of slurry volume. *Materials*. 2021, vol. 14, p. 6940.

[14] SIENKIEWICZ, J., KURODA, S., MURAKAMI, H. et al. Fabrication and oxidation resistance of TiAl matrix coatings reinforced with silicide precipitates produced by heat treatment of warm sprayed coatings. *J Therm Spray Tech.* 2018, vol. 27, pp. 1165–1176.

[15] HIGHTOWER, A., FULTZ, B. BOWMAN, R.C. Mechanical alloying of Fe and Mg. *Journal of Alloys and Compounds.* 1997, vol. 252, pp. 238-244.

[16] DOROFEEV, G.A., ELSUKOV, E.P., ULYANOV, A.L. Mechanical alloying of immiscible elements in the Fe–Mg System. *Inorganic Materials.* 2004, vol. 40, pp. 690–699.

[17] SURYANARAYANA, C. Mechanical alloying: a critical review. *Materials Research Letters*. 2022, vol. 10, pp. 619-647.

[18] PHILPOT, K.A., MUNIR, Z.A., HOLT, J.B. An investigation of the synthesis of nickel aluminides through gasless combustion. *J. Mater. Sci.* 1987, vol. 22, pp. 159–169.

[19] SARKISYAN, A.R., DOLUKHANYAN, S.K., BOROVINSKAYA, I.P., MERZHANOV, A.G. Laws of the combustion of mixtures of transition metals with silicon and the synthesis of silicides. *Combust., Explos. Shock Waves (Engl. Transl.)*. 1978, vol. 14, pp. 310–314.

[20] MASSALSKI, T.B. *Binary alloy phase diagrams*. ASM International, Materials Park, Ohio, 1990.