Archives of Materials Science and Engineering

Volume 28
Issue 11
November 2007
Pages 673-676

International Scientific Journal
published monthly as the organ of
the Committee of Materials Science
of the Polish Academy of Sciences

Consolidating condition of Cr-Si compacts and their microstructure

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Received 11.10.2007; published in revised form 01.11.2007

ABSTRACT

Purpose: Determine the possibility of production of CrSi compacts from Cr and si elemental powders.

Design/methodology/approach: The CrSi compacts containing 0.5, 1, 2, 3, at. % of Si were prepared from elemental powders (crystallites size:Cr;1-5 μm and Si;45 μm) by mixing and hot pressing at 1600°C under ~25MPa. The microstructure was characterized using optical, SEM and TEM.

Findings: The matrix of the compacts containing silicon show presence of dendrite like areas filled with eutectic like mixture of amorphous SiO_2 and crystalline CrOx. The dendrite volume increase from 0.7% to 2% for Cr0.5Si to Cr3Si compacts respectively.

Research limitations/implications: (Please leave in the title a suitable word); (Could you please put your information in this box): If research is reported in the paper this section must be completed and should include suggestions for future research and any identified limitations in the research process.

Practical implications: The described experiments advice on preparation of dense CrSi compacts from elemental powders. It may be used as technology of producing magnetron targets for deposition of hard coatings like CrN/Si_3N_4.

Originality/value: The paper is answering the problem, i.e. describes the optimum parameters, of obtaining of the multi-elemental coating in single target magnetron systems.

Keywords: Metallography; CrSi compacts; Hot pressing; Microstructure; Optical microscopy

METHODOLOGY OF RESEARCH, ANALYSIS AND MODELLING

1. Introduction

The wide introduction of two or three target magnetron systems in recent years allowed to start experiments toward deposition of new multi-element coatings like nc-TiN/a-Si_3N_4, nc-CrN/a-Si_3N_4 or nc-TiC/a-C(Al) nano-composites impossible to obtain with one target systems [1, 2, 3].

These advanced magnetrons are especially well suited for research conducted at laboratories as they allow high flexibility as it concerns steering the coating composition by simple power adjustments on separate targets. Simultaneously, high cost of such systems, complicated operation as well as inter-target poisoning during longer run, rather exclude them from wider industrial application. The way out from this situation is to try to produce composite targets, which may help to produce multi-element coatings of predetermined composition using single target magnetron. The composite targets should be characterized by a low porosity, which otherwise may adversely influence power transfer lowering deposition rate. Additionally, they should be highly homogenous, as the preferential etching in plasma may result in unspecified composition shift between that of target and the coating.

The previous experiments with hot compacting of titanium and silicon powders of 150 and 200 μm mesh respectively allowed to

obtain dense targets nominally containing 4, 6 and 10 at.% Si [4]. However, coarse powders chosen to keep the technology commercially acceptable resulted in limited dissolution of silicon in titanium matrix max. up to 2 at.% and frequent presence of non-reacted silicon crystallites surrounded by a layer of silicon rich phase. The preferential etching of silicon crystallites was probably the reason that coatings showed from 1 - 2 at.% higher silicon content, than their respective nominal target composition [5]. Never the less the deposited nano-composite TiN/Si_3N_4 coatings produced with the TiSi4 target showed hardness exceeding that characteristic for TiN and allowed to extend significantly the tool lifetime [6].

The further improvement in this direction is expected by substituting titanium with chromium as CrN is only slightly less hard than TiN, while much more resistant to degradation at high temperature prevailing at cutting tools working conditions. The experiments performed using double magnetron systems confirmed that CrN coatings with silicon additions also increase their hardness reaching maximum hardness with Si content between 2 and 4 at.% [3]. Considering Ti-Si composite targets it seems of interest to investigate the possibility of producing Cr-Si compacts serving as magnetron targets for development of low cost technology of deposition of CrN/Si_3N_4 nano-composite coatings. It is expected that, using the above approach multi-component magnetron targets might be produced extending application of the magnetron technique in coatings produced up till now with other techniques [7-9]. Simultaneously, having in mind longer target use and preservation of constant coatings composition it seems necessary to eliminate the non-reacted silicon crystallites.

The aim of the present paper was to summarise the first attempts on elaboration of conditions of production of dense Cr-Si compacts and describe their microstructure.

2. Material and compacting procedure

The Cr-Si compacts containing 0,5, 1, 2, 3 at.% of Si were prepared from elemental powders (from 1 to 5 μm in case of chromium crystallites and of ~45 μm average crystallite size for silicon) mixed and hot pressed. The compacting conditions including temperature, pressure and piston travel distance with time are presented in Fig. 1. The pressure was increasing in linear way up to 4T of load (~25 MPa) after ~35 min. The maximum temperature of 1600°C was achieved after 100 minutes and next kept for additional 40 minutes. The third stepped curve shows the piston travel and illustrates the sinter densification. Analysis of the information given by these curves indicates that densification was finished already at 1300°C. The above process performed in a graphite die in argon atmosphere allowed to produce compacts of final dimensions ϕ~50 mm and thickness ~6 mm.

3. Characterization procedure

Microstructure investigations were performed using Leica optical microscope (OM), FEI xL30 scanning microscope (SEM) and FEI TECNAI FEG transmission electron microscope (TEM) with integrated EDAX microanalysis attachment.

The sample for OM and SEM observations were polished or etched. The thin foils for TEM observations were prepared using focus ion beam (FIB) technique [10-12] with FEI Quanta system. The images quantification was performed using Leica software [13].

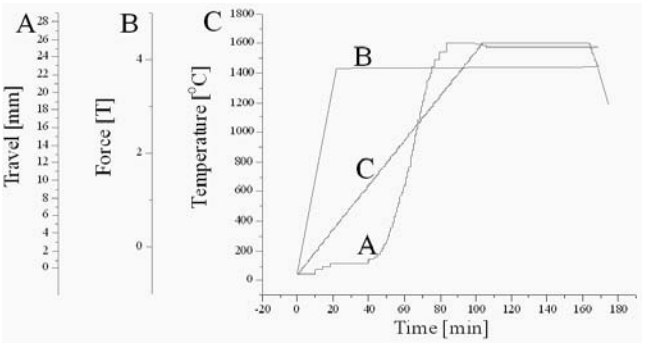

Fig. 1. Compacting conditions of Cr-2at.% Si sinter

4. Microstructure observation results

Fig. 2 presents scanning microstructure of polished surfaces of Cr, Cr-1at.%Si and Cr-3at.%Si compacts. The Cr compacts gives an estimate of the pores and oxides agglomerates unavoidably at such sintering conditions. The Cr-1at.%Si and Cr-3at.%Si show also presence of dendrite like objects. In case of the compact with up to 1a % Si they exist in a form of separate arm like structures, while compacts with 2 and 3 at.% Si show presence of small colonies (one example marked with broken circle).

The quantitative assessment of scanning microstructure of Cr compact polished surfaces indicated that the pores and agglomerates of contaminating oxides amounts in it up to ~3 vol. % and stay at that level also in compacts with increasing silicon addition (Table I). On the other hand, the presence of dendrite phase was increasing with rising silicon content (Table 1 and Fig.3). Optical microscopy observations of etched compacts surfaces revealed grain size within the 30 – 150 μm range. Additionally, they showed that even as distribution of pores and dendrites is roughly homogenous, though they evidently tend to form at grain boundaries (Fig.4).

Table 1.
Quantitative estimation of volume fraction of summed voids and oxides as well as dendrite phase in Cr-Si compacts

Compacts	Cr	Cr-0,5at.% Si	Cr-1at. %Si	Cr-2at. %Si	Cr-3at. %Si
voids+oxides	3,6	3,2	3,5	3,4	3.7
"dendrities"	0	0,7	1,1	1.8	2

The higher magnification observations using again scanning microscopy showed a eutectic type microstructure inside dendrite like areas (Fig. 5). The transmission electron microscopy observations of thin foils cut using Ga+ focused ion beam (FIB) technique confirmed, that it is indeed a two phase area. The vertical low contrast smudges are sample preparation artifacts resulting from different sputtering rate of materials present in eutectic like region. One of the eutectic constituent was found crystalline, while the other (the light gray) was amorphous as proved using electron diffraction technique (Fig. 6).

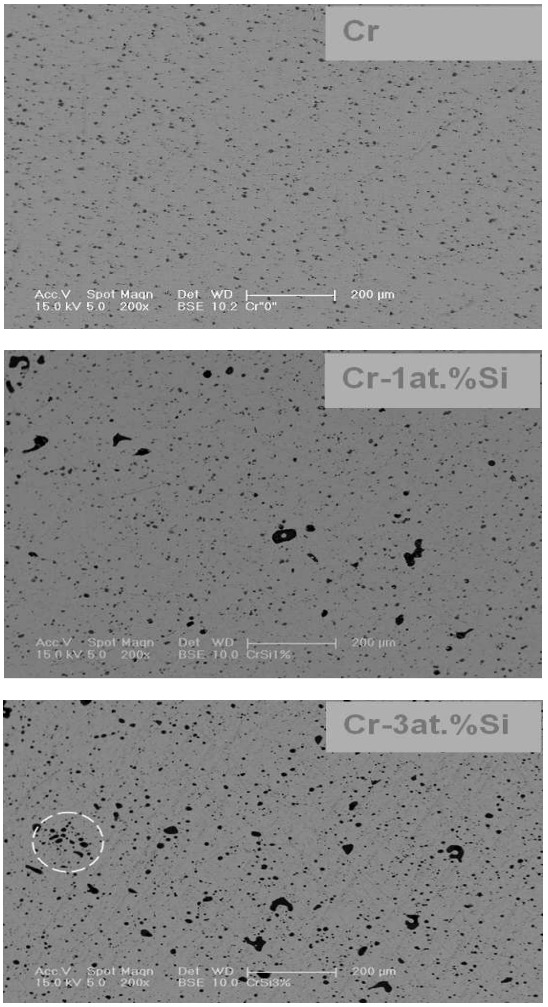

Fig. 2. SEM image of Cr, Cr-1at.%Si and Cr-3at.%Si compacts

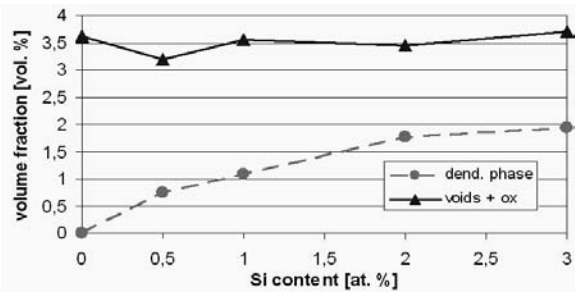

Fig. 3. Changes in volume of "voids and oxides" and eutectic like structure in Cr-Si compacts with up to 3 at.% Si

The qualitative local chemical analysis performed using EDS attachment were taken from points 1 to 4 as marked in Fig. 7 and presented in Fig. 8.The first spectra obtained from the matrix showed only presence of chromium indicating small dissolution of silicon in it. The analyses of crystalline phase from dendrite areas shows lower Cr_Kα line intensity and much stronger Cr_Lα due to overlap with O_Kα line. This phase, therefore, was identified as CrO_x. Only occasionally from regions with characteristic striations a spectra with Cr and Si was acquired. The amorphous phase in-between the crystalline veins was identified as silicon oxide.

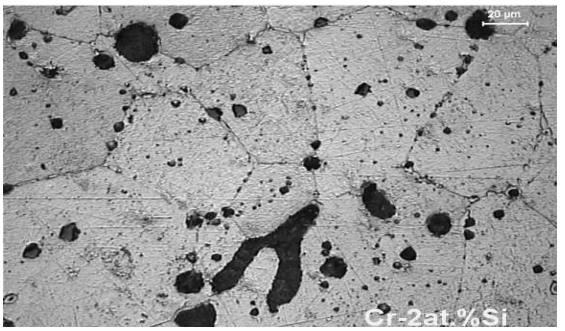

Fig. 4. Optical image of etched surface of Cr-2at.%Si compacts

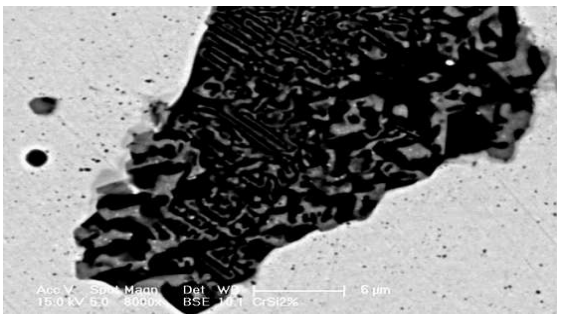

Fig. 5. SEM image of inside of dendrite like areas (Cr-2at.%Si)

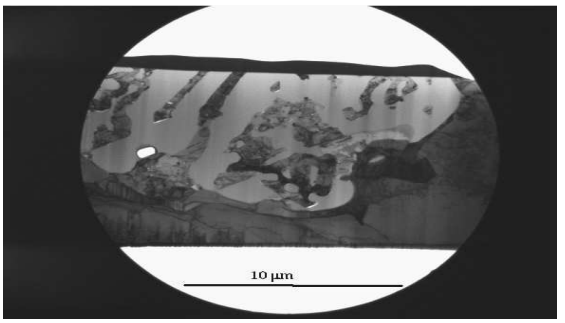

Fig. 6. TEM image of FIB thin foil cut from dendrite area from Cr-2at.%Si compact

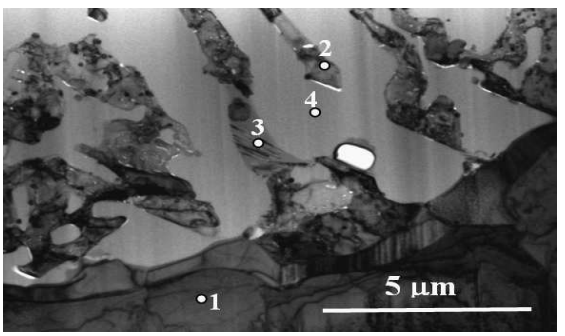

Fig. 7. TEM image of eutectic microstructure of dendrite areas (places of EDS analyses marked with 1, 2, 3 and 4) from Cr-2at.%Si compact

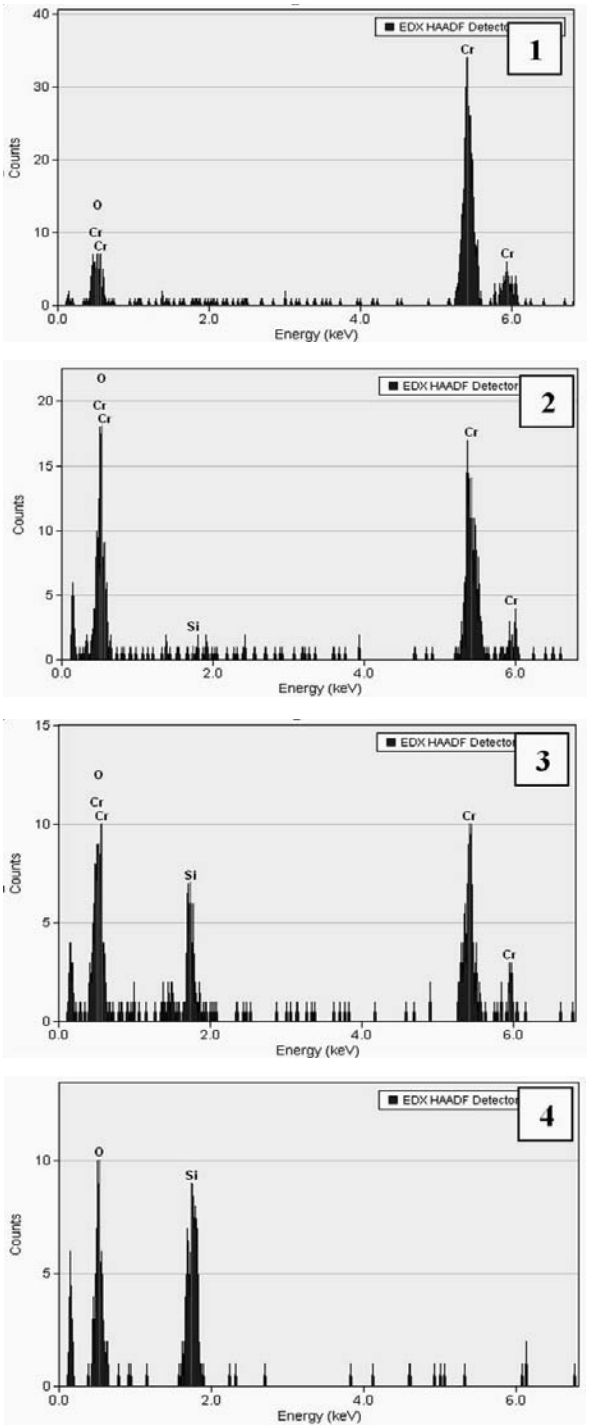

Fig. 8. EDS spectra obtain from point marked on Fig. 7

5. Conclusions

1. The consolidating of mixed chromium and silicon powders at 1600°C under ~25 MPa pressure allowed producing dense compacts with up to 3 at. % Si.
2. The strong grain growth observed in Cr and CrSi compacts up to size of 200 μm suggest a possibility of shortening compacting time.
3. All compacts presented similar ~3 vol. %porosity, while the size of dendrite areas increases with rising silicon content from 0,7 to 2 vol. % for Cr-0,5Si to Cr-3Si compacts respectively.
4. The dendrite regions turned out to contain mostly a eutectic like mixture of amorphous silicon oxide and crystalline chromium oxide. The Cr-Si phases were also detected but only as minority fraction.

Acknowledgements

The support through Polish Ministry of Science and Education Project no PW-004/ITE/04/2006/1.1 Development of nanotechnology in surface engineering is acknowledged

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