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EFFECT OF 5 AT. % ADDITION OF Cr, V AND W ON MICROSTRUCTURE AND MECHANICAL PROPERTIES OF γ-TiAl BASED ALLOYS

WPŁYW 5% AT. DODATKU Cr, V I W NA MIKROSTRUKTURĘ I WŁASNOŚCI MECHANICZNE STOPÓW NA OSNOWIE γ-TiAl

Alloys with chemical compositions TiAl48, TiAl45Cr5, TiAl45V5 and TiAl45W5 were synthecised by mechanical alloying. The compaction of powders was perform by hot pressing (pressure sintering) at 1300°C and pressure 25 MPa or by hot isostatic pressing at pressure of 1.4 GPa. Hot isostatic pressing produced alloys with exceptionally high yield strength approaching 2.5 GPa along with satisfactory ductility and fracture toughness. On the other hand, the consolidation of powders at low pressure turned out to be not an adequate compaction method for the produced alloys. The produced alloys were formed mostly by the expected phases (γ and α_2-based ones), however, their chemical composition departed from stoichiometry.

Keywords: intermetallics, TiAl, mechanical alloying

W pracy wytworzono i badano stopy o następujących składach chemicznych: TiAl48, TiAl45Cr5, TiAl45V5 oraz TiAl45W5 (% at.). Jako metodę wytwarzania wybrano mechaniczną syntezę proszków czystych metali. Konsolidację proszków przeprowadzono poprzez prasowanie na gorąco (spiekanie pod ciśnieniem) w temperaturze 1300°C i przy ciśnieniu 25 MPa oraz przez izostatyczne prasowanie na gorąco przy ciśnieniu 1,4 GPa. Stopy poddane izostatycznemu prasowaniu na gorąco wykazywały wyjątkowo dużą granicę plastyczności dochodzącą do 2,5 GPa przy zachowaniu zadowalającej ciągliwości i odporności na pękanie. Prasowanie na gorąco przy małym ciśnieniu prowadziło do wytworzenia stopów o znacznie gorszych właściwościach. Produkowane stopy zbudowane były zgodnie z oczekiwaniami z faz na osnowie γ i α_2, lecz ich skład chemiczny odbiegał od składów stechiometrycznych.

1. Introduction

The Ti-Al alloys are considered as potential high temperature engineering materials for over two decades. This is due to their attractive weight-specific properties and high-temperature capacities. However, there is still significant need for improvement of their properties such as ductility, fracture toughness and high temperature creep resistance. Much progress has been made in our understanding of the relationship between microstructure and mechanical properties, whereas some obstacles remain to be overcome [1, 2]. Since single phase γ-TiAl alloys exhibit these inherent shortcomings and due to a lack of progress toward overcoming their poor ductility and fracture toughness, the interest has been concentrated in recent time on the development and optimization of two phase alloys [3, 4]. These consist of γ-TiAl with face-centered tetragonal $L1_0$ crystal structure as main component and minor amount of α_2-Ti_3Al ($D0_{19}$ hexagonal crystal structure). Microstructures of two-phase γ-TiAl alloys may be classified into four groups: near gamma, duplex, nearly lamellar and fully lamellar. All types of microstructures have a significant effect on mechanical properties. For example, a duplex structure can improve the tensile ductility, while fracture toughness and creep strength are improved by a lamellar microstructure [3]. It has been also concluded recently that major overall improvement in the properties of these unique alloys may be achieved by alloying and application of non-standard processing methods.

This research was aimed on the production of fine-grained two-phase TiAl materials by mechanical alloying (MA) followed by different powder consolidation methods. In particular, the influence of minor addition of Cr, V and W as well as the consolidation method on microstructure and thus mechanical properties was investigated. MA offers the advantages of refining the grain sizes and the generation of non-equilibrium phases. Also,

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the controlled oxygen level in milling chamber produces oxide dispersoid which contribute to the improvement of strength and creep properties despite fine-grained microstructure.

2. Material and experimental procedure

The alloys with the following compositions (in at.%) were synthecisized by mechanical alloying: TiAl45Cr5, TiAl45V5, TiAl45W5 and TiAl48 as a referenced material. The excess of titanium with respect to stoichiometry in all alloys was supposed to assure that the alloys will exhibit two-phase microstructure. The details of the MA process are described elsewhere [5]. The amount of powder produced in one run of the mill was usually 200-300 g. The powders collected at the end of milling were sieved through a 44 μm mesh and consolidated by hot pressing (HP) at 1300°C and 25 MPa in an argon atmosphere for 3 h. The alloys TiAl45V5 and TiAl45W5 were also consolidated by hot isostatic pressing (HIP) at 1100°C and 1200°C at 1.4 GPa for 14 h. The compacted materials were subjected to XRD analysis. Microstructure of the consolidated material was characterized by SEM with utilization of the Z contrast produced by BSE and also by TEM. Both electron microscopy techniques were supplemented by the energy dispersive spectrometry (EDS). The measurements of chemical compositions of constituent phases, both in SEM and TEM, were performed by a standardless method which total all elements to 100%. Light elements analysis was not performed. In order to examine distribution of oxide dispersoid metallographic sections were also subjected to light microscope investigations.

Mechanical tests comprised determination of elastic constants, hardness and compression yield strength at room temperature. Samples of the TiAl48, TiAl45Cr5 and TiAl45V5 alloys consolidated by hot pressing at 1300°C and 25 MPa were subjected to compression tests at 700, 800 and 900°C. Evaluation of fracture toughness K_{Ic} was performed from microcraks propagating from Vickers indentation corners on the prepolished sample surfaces. For this purpose the Palmquist [6] model of microcracks formation and mathematical analysis proposed by Niihara et al. [7] were adopted.

3. Results and discussion

Microstructure

The current alloys produced by mechanical alloying and HP or HIP densification have a satisfactory quality. XRD patterns from the consolidated materials were almost identical with those from the annealed powders [5]. The only difference was in breadth of diffraction peaks: the peaks from consolidated samples were broader, due to likely fine grain microstructure and stresses arising from different coefficient of thermal expansion of particular phases (Fig. 1).

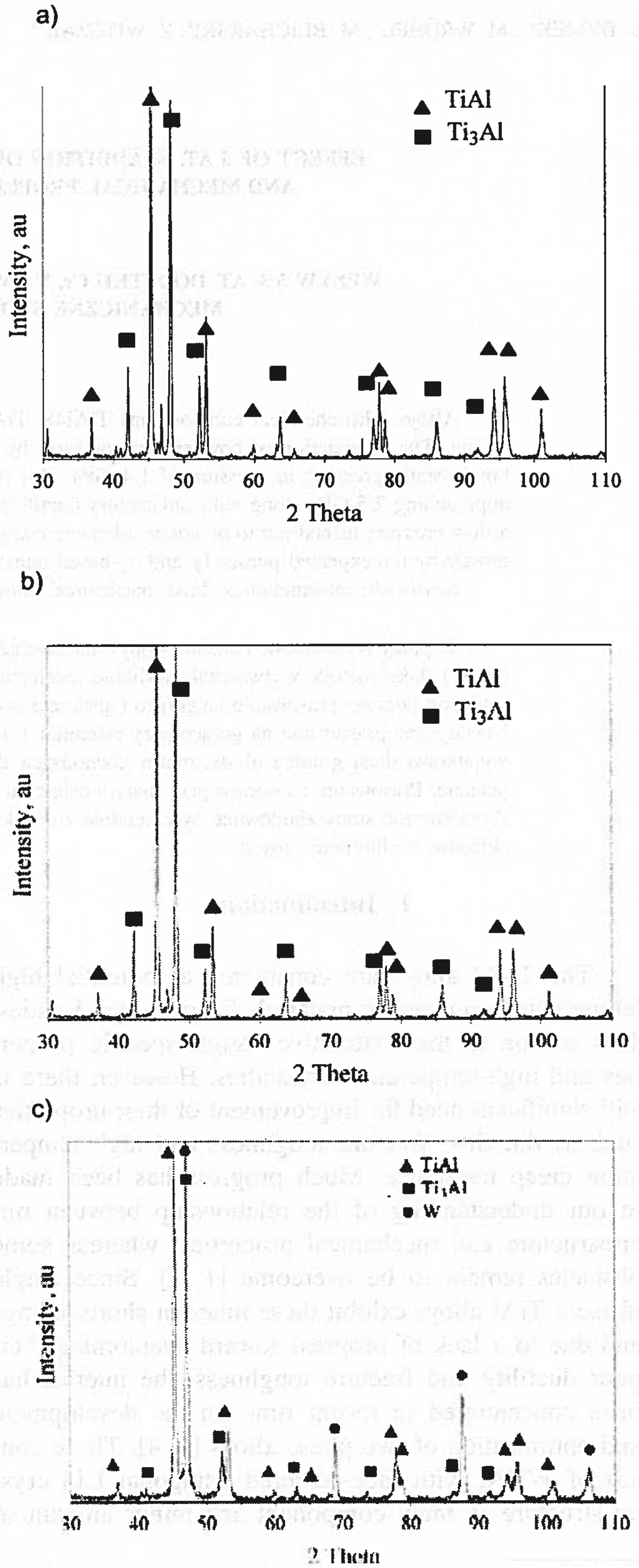

Fig. 1. XRD paterns from consolidated materials: a) TiAl5Cr alloy, b) TiAl5V alloy, c) TiAl5W alloy

Optical microscopy allowed the distribution of oxide particles to be revealed (Fig. 2). The distribution was fairly uniform throughout the sample. The phases detected by X-ray analysis were also revealed in SEM images formed by backscattered electrons with utilization of Z-contrast (Fig. 3). Such images are particularly useful in determination of size and distribution of constituent phases. Black particles in Fig. 3 contained mainly aluminum and oxygen (with at. % ratio 2 : 3) and thus were identified as Al_2O_3. SEM investigation confirmed that the distribution of oxides in all alloys was more or less uniform, however, in the TiAl45Cr5 alloy well defined bimodal distribution of oxides was found: among relatively big oxides the nano-sized particles were observed (Fig. 3). Beside oxides, the microstructure was composed of areas with different degree of grayness: brighter areas contained more Ti than Al (in at. %) while in the darker one the Ti and Al contents were similar. Taking into account X-ray phase analysis, the darker and brighter areas were identified as phases based on Ti_3Al and TiAl, respectively. The interesting finding in the present research is that the produced alloys did not exhibit a lamellar microstructure which is typical for the two-phase γ-TiAl-based alloys with similar chemical composition but synthesized by different methods [8, 9]. The lamellar microstructure was found sporadically and only in the alloy with Cr.

Fig. 2. Optical microstructure of TiAl45V5 alloy after consolidation by hot pressing at 1300°C and 25 MPa

TEM investigation, along with selected area diffraction patterns analysis, confirmed that the examined alloys constituted the mixture of Ti_3Al-based and TiAl-based phases. Both phases were built of colonies of grains, however, the chemical compositions varied in particular alloys and particular grains belonging to the same phase. Though the Ti:Al atomic ratio in the TiAl-based phase was close to 1:1 in each examined alloy, the grains with excess of Ti prevailed. The content of a third element in this phase was different in particular alloys. In the TiAl45V5 alloy, V was partitioned evenly to both phases and its content was near the targeted value of 5 at. %. In the TiAl45Cr5 alloy, the fairly large scatter in Cr content in both TiAl- and Ti_3Al-based phases was observed but never went above 4.5 at. %. It means that not less than 0.5% Cr must have precipitated as other phases not detected by X-ray phase analysis. It is very likely that the nano-sized particles observed in SEM BSE images are a Cr-rich phase. Moreover, a phase with B2 crystal structure might have appeared in this alloy since Cr favors nucleation of this phase and stabilizes it [10]. Also, not less likely is an occurrence of a brittle ω phase which was found in TiAl-Cr alloys [11]. The occurrence of Cr-rich phase in microstructure may be justified since XRD pattern of the TiAl45Cr5 powder after 100 h of milling showed a well-defined peak from the Cr-based solid solution [5]. However, such a phase was not detected by XRD or electron microscopy studies.

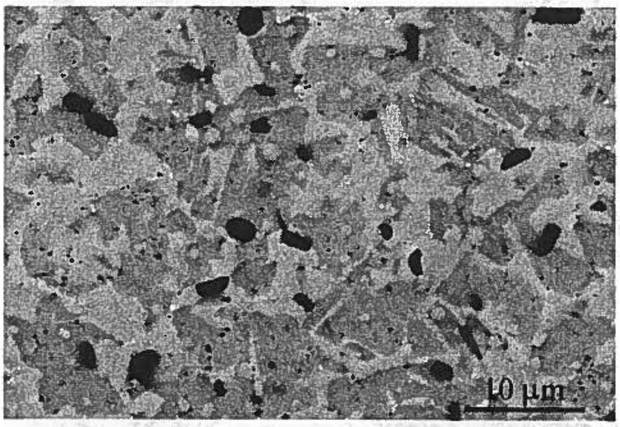

Fig. 3. Typical microstructure of the TiAl45Cr5 alloy; SEM BSE, contrast Z: bimodal distribution of oxide particles in the alloy

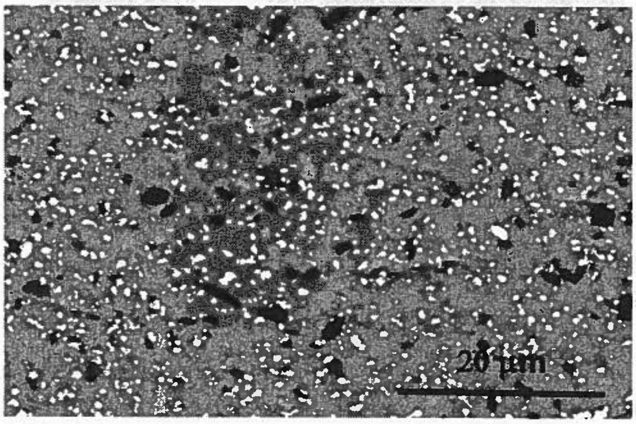

Fig. 4. Typical microstructure of the TiAl45W5 alloy; SEM BSE, contrast Z; white particles represent tungsten

The chemical composition of the Ti_3Al-based phase was far from stoichiometry in all examined alloys, with Ti content ranging from 57 to 67 at. %. The presence of the Al-rich Ti_3Al-based phase is detrimental to mechanical properties of these alloys since it is considered as a primary source of brittleness at room temperature [12]. Vanadium went easily into Ti_3Al solid solution while the chromium content differed largely in particular grains. Even grains with an amount of Cr as low as 0.15 at. % (a value within the error limits) were found in this phase. Tungsten did not dissolve in neither phase and formed small W-rich precipitates uniformly distributed in both phases (Fig. 4).

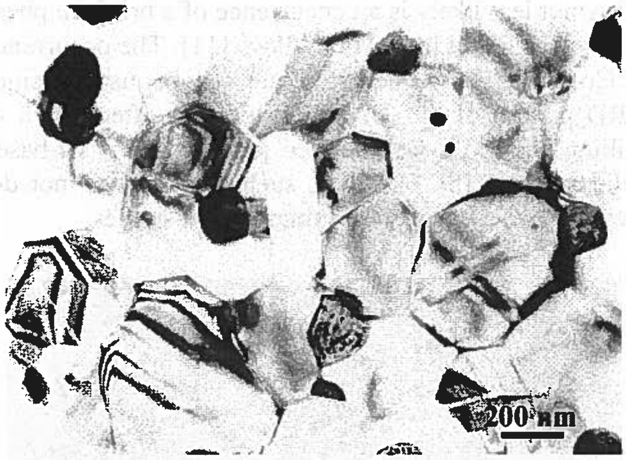

Fig. 5. Typical microstructure of the TiAl45W5 alloy consolidated by HIP; TEM

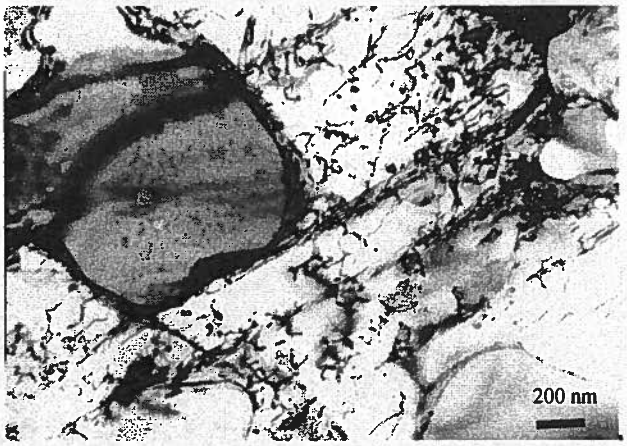

Fig. 6. Typical microstructure of the TiAl45W5 alloy consolidated by HP; TEM

TEM examinations revealed pronounced differences in microstructure for differently consolidated materials. The first striking difference is in grain size: in the HIP materials the grain size was about 0.5 μm and well recrystallized (Fig. 5) while in the hot pressed ones the grain size was well above 1 μm and the substructure is typical for post-deformed samples with numerous dislocations and deformation twins (Fig. 6).

Mechanical properties

Density and elastic constants of consolidated materials are collected in Table 1. Basic mechanical properties at room temperature are placed in Table 2. Compression yield strengths at elevated temperatures of TiAl48, TiAl45Cr5 and TiAl45V5 alloys consolidated at 1300°C at 25 MPa are shown in Table 3. The yield strength of all hot pressed materials was higher than in other γ-TiAl alloys with similar chemical compositions which is usually in the range of 360-450 MPa depending on microstructure [9]. It is clear that all physical and mechanical properties depended not only on chemical composition but also on consolidation method. Porosity of HIPed materials is much lower comparing to hot pressed ones. A ductile behavior was observed in all HIPed materials together with a relatively high yield stress (Fig. 7). However, the ductility took place without any considerable strain hardening. The alloy TiAl45V5 consolidated at 1100°C showed the highest yield stress, about 2500 MPa. The same alloy consolidated at 1200°C exhibited lower yield stress but its ductility was much better.

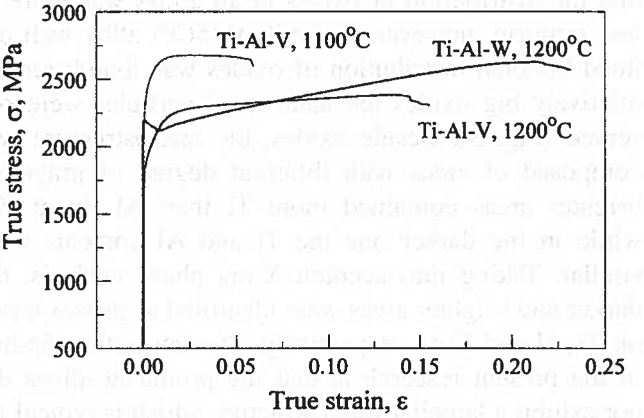

Fig. 7. Stress-strain curves for alloys consolidated by HIP and deformed at room temperature

TABLE 1

Density and elastic constants of consolidated materials

Material/consolidation	Density, g/cm^3	Young modulus, GPa	Poisson number
TiAl48 HP 1300°C	3.89	168	0.21
TiAl45Cr5 HP 1300°C	3.94	178	0.24
TiAl45V5 HP 1300°C	3.91	179	0.22
TiAl45V5 HIP 1200°C	4.00	179	0.26
TiAl45V5 HIP 1100°C	3.99	175	0.26
TiAl45W5 HP 1300°C	4.42	180	0.15
TiAl45W5 HIP 1200°C	4.54	194	0.23

The hot pressed materials showed very limited ductility at room temperature – below 1% in compression. Much better mechanical properties of HIPed alloys are undoubtly associated with their different microstructure: grains in these alloys were smaller (< 1 μm) and almost dislocation free. The dislocation density in hot pressed alloys was relatively high, what might be a reason of much lower yield strength.

TABLE 2

Mechanical properties at room temperature

Material/consolidation	Hardness, HV	Yield strength, MPa	K_{Ic}, $MPa \cdot m^{0.5}$
TiAl48 HP 1300°C	400	615	12
TiAl45Cr5 HP 1300°C	430	823	9
TiAl45V5 HP 1300°C	600	861	3
TiAl45V5 HIP 1200°C	613	1800	*
TiAl45V5 HIP 1100°C	630	2500	5
TiAl45W5 HP 1300°C	380	not tested	*
TiAl45W5 HIP 1200°C	550	2200	*

* no microcraks were produced at indent corners

TABLE 3

Compressive yield strength in MPa at elevated temperatures of TiAl48, TiAl45Cr5 and TiAl45V5 alloys consolidated at temperature 1300°C and pressure 25 MPa

Material	Temperature, °C		
	700	800	900
TiAl48	346	173	27
TiAl45Cr5	682	476	112
TiAl45V5	712	457	98

The highest yield stress found so far in γ-TiAl-based alloys was around 2.5 GPa. It was reported by Bohn et al. for a TiAl48 alloy with a grain size around 130 nm [13] and by Calderon et al. for a nanocrystalline TiAl46Cr4 alloy produced also by mechanical milling but consolidated by spark plasma sintering – the method which makes possible to obtain a nanostructure in bulk materials due to short processing times [14]. The present TiAl45V5 and TiAl45Cr5 alloys consolidated by HIP show also the exceptionally high flow stresses without having a lamellar microstructure. The refinement of a lamellar microstructure gives usually rise to an increase of yield strength in γ-type alloys [1]. The high values of yield strength obtained in the present reaserch are certainly associated with the alloying additions, fine grain size as well as the presence of oxide dispersoid.

The refinement of grain size plays also a critical role in ductility improvement, not only in current alloys but in other intermetallics as well [15]. According to Cottrell concept [16], there is a critical grain size below which the yield strength becomes lower than the stress necessary to propagate microcraks and therefore the increase in ductility is observed.

The presence of alloying addition not only increases yield strength at room temperature but also influences its retention at elevated temperatures. However, all materials tested at high temperatures exhibited sudden drop in yield strength at 900°C; such behavior is typical for all Ti-based alloys [8, 9].

Hardness of the examined materials differ in particular alloys and seems to be not correlated with yield strength. Similar conclusion may be drawn out about fracture toughness which depends mainly on the consolidation method.

4. Conclusions

1. Mechanical alloying followed by hot isostatic pressing of powders at high pressure of 1.4 GPa can be used to produce the TiAl-X (X=Cr, V, W) alloys with exceptionally high yield strength and satisfactory ductility and fracture toughness. On the other hand, the consolidation of powders at low pressure is not an adequate compaction method.
2. The produced alloys are formed mostly by the expected phases (TiAl- and Ti_3Al -based ones), however, their chemical composition departs from stoichiometry.

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REFERENCES

[1] F. Appel, R. Wagner, Mat. Sci. Eng. **R22**, 187 (1998).

[2] H. Clemens, H. Kestler, Adv. Eng. Mater. **2**, 551 (2000).

[3] Y.-W. Kim, D. M. Dimiduk, Journal of Metals **43**, 40 (1991).

[4] Y.-W. Kim, Journal of Metals **46**, 30 (1994).

[5] To be published in Archives of Metallurgy and Materials, 2006.

[6] S. Palmquist, Jernkontorets Ann. **141**, 300 (1957).

[7] K. Niihara, R. Morena, D. P. H. Hasselman, J. Amer. Ceram. Soc. **65**, C-116 (1982).

[8] S. C. Huang, J. C. Chesnutt, Intermetallic Compounds **2**, ed. J. H. Westbrook, R. L. Fleischer, John Wiley Sons Inc., 1995, p. 73.

[9] F. H. Froes, C. Suryanarayana, in: Physical Metallurgy and Processing of Intermetallic Compounds, ed. N. S. Stoloff and V. K. Sikka, Chapman & Hall, 1996, p. 297.

[10] R. Kainuma, I. Ohnuma, K. Ishikawa, K. Ishida, Intermetallics **8**, 869 (2000).

[11] G. Shao, P. Tsakiropoulos, Acta Mater. **48**, 3671 (2000).

[12] Y. L. Hao, R. Yang, Y. Y. Cui, D. Li, J. Mater. Sci. Technol. **15**, 536 (1999).

[13] R. Bohn, T. Klassen, R. Bormann, Acta Mater. **49**, 299 (2001).

[14] H. A. Calderon, V. Garibay-Febles, A. Cabrera, N. Motta-Solis, M. Umemoto, M. Yamaguci, Structural Intermetallics 2001, ed. K. J. Hemker et al., TMS 2001, p. 683.

[15] M. Dollar, S. Dymek, S. J. Hwang, P. Nash, Metall. Trans. **24A**, 1993, (1993).

[16] A. H. Cottrell, Trans. AIME **212**, 192 (1958).

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